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A REVIEW OF RECENT DETERMINATIONS OF THE COMPOSITION AND SURFACE PRESSURE OF THE ATMOSPHERE OF MARS

*by M. W. P. Cann, W. O. Davies,
J. A. Greenspan, and T. C. Owen*

Prepared under Contract No. NAS 5-9037 by
IIT RESEARCH INSTITUTE
Chicago, Ill.
for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C.





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PREFACE

This study was undertaken in response to a NASA request for an evaluation of the experimental data and theoretical analyses on which current estimates of the Martian surface pressure are based. A previous NASA-sponsored review of this same subject has been prepared by Chamberlain and Hunten. We have been able to include a discussion of several recent papers which were not available at the time of the Chamberlain-Hunten report and have investigated some of the subjects common to both studies in somewhat greater detail. Some topics have been well-covered by Chamberlain and Hunten and are consequently considered only briefly (or omitted) here.

The present report was written in two stages. The preliminary draft included much of the numerical work that led to the results reported in this version. Subsequent to its completion, a visit to Dollfus was arranged which led to a substantial revision of our review of his work. The preliminary report was submitted to the following consultants for review: Drs. J. W. Chamberlain and D. M. Hunten (Kitt Peak National Observatory), Dr. J. Strong (Johns Hopkins University), Dr. S. L. Hess (Florida State University), Dr. K. L. Coulson (General Electric Co.), and Dr. W. S. Benedict (Johns Hopkins University).

The comments of these consultants have been most helpful in preparing the final version of this report and it is a pleasure to acknowledge their assistance. Their criticisms have led, in some instances, to alterations in the preliminary manuscript, while in other cases we have included specific (referenced) comments because of the insight they furnish on particular points. The views expressed in this final version do not necessarily represent a consensus of the listed consultants, however, since different parts of the report received more attention by some reviewers than by others.

We would also like to express our thanks to the scientists whom we have contacted in the course of our review: Dollfus, Focas, Goody, Hanst, Inn, Kaplan, Kuiper, Münch, Rank, Sinton, and Spinrad. Their patience and willingness to discuss their work is gratefully acknowledged. Particular thanks are due to Dollfus, Kaplan, and Rank for their hospitality and generous donation of time during the course of personal visits.

We are indebted to Miss P. Brunsting for her valuable assistance in the preparation of the manuscript.

ABSTRACT

This study presents a review of recent determinations of the Martian surface pressure. A brief historical survey of the subject is presented in the introduction. The polarimetric work of Dollfus is discussed in Section 2 and a new value of the surface pressure (63 mb) is derived from his data making use of more recent photometric data and of a new treatment of the angular dependence of the planetary surface brightness. A photometric argument presented by Musman is also discussed, and the general effects of aerosols and various mixtures of gases on the pressure estimates are investigated. It is shown that these lead to a range of pressures depending on the assumptions made, and that this method of pressure determination consequently leads to indeterminate results.

Section 3 reviews the spectroscopic work of Kaplan, Münch, and Spinrad; Owen and Kuiper; Hanst and Swan; and Moroz. A value of 45 ± 25 m-atm for the Martian CO₂ abundance is derived from these papers, corresponding to a mean Martian atmospheric temperature of 200°K. Using this abundance, the various methods used by the different authors for estimating the surface pressure are reviewed, leading to surface pressures ranging from 13 to 33 mb with relative errors on the order of

$\pm 90\%$. The large uncertainty is primarily a result of the fact that the abundance determination rests on the measurement of three weak lines in a single spectrogram.

A summary of the report and its final conclusions are presented in Section 4. A collection of appendices follows the concluding section and is designated as Part II of the report. The appendices contain some of the calculations supporting the results presented in Part I as well as elaborations of certain topics which are only briefly treated in Part I.

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1. INTRODUCTION

The specific problem which is considered in this report is the apparent inconsistency between the value of the surface pressure of the Martian atmosphere which has been determined from photometric and polarimetric studies (85 mb) and the figures derived from recent spectroscopic observations (10-40 mb). This inconsistency has been particularly disturbing to those responsible for the design of spacecraft or capsules which would be used in an attempt to reach the surface of the planet, since the range in surface pressure covered by this uncertainty would have a definite influence on the aerodynamic design of the entering vehicle. It is perhaps worthwhile to present a brief chronological summary of the various observations and interpretations which have led to the current controversy.

The value of the surface pressure which has been generally accepted is 85 mb, a number which rests primarily on polarimetric observations made by A. Dollfus. The principal reason for the acceptance of this number appears in retrospect to have been the small probable error (± 4 mb) assigned to it by de Vaucouleurs¹ in a book which has been widely read by those interested in Martian problems. This probable error was based on the apparent consistency of four semi-independent methods used by Dollfus to determine the ratio of the

atmospheric to surface brightness on Mars. Additional grounds for supporting this value were provided by its near agreement with results obtained photometrically by de Vaucouleurs himself.

The previous discovery of CO_2 in the atmosphere of the planet in 1947 by Kuiper⁷ was not in any way contradictory to this result. Kuiper interpreted his observations with the help of a curve of growth of the telluric CO_2 bands and derived a Martian CO_2 abundance of 4.4 m-atm. Grandjean and Goody⁸ pointed out that the amount of CO_2 in the Martian atmosphere implied by Kuiper's observations required a consideration of the pressure difference between the Earth's atmosphere and that of Mars, but they relied on a Martian surface pressure of roughly 100 mb for their interpretation (although they included calculations for 50 mb and 150 mb as well). They derived a value of 30 m-atm for the Martian CO_2 abundance using the 100 mb surface pressure.

Kuiper⁷ pointed out that the presence of small particles in the Martian atmosphere, which would act as Rayleigh scatterers at the wavelengths at which Dollfus made his observations, would mean that the atmospheric pressure derived from the polarimetric observations would be an upper limit. He suggested that the "blue haze" (a well known Martian atmospheric phenomenon) might be caused by such particles. The effect of scattering particles in reducing the surface pressure estimate was also pointed out by Goody⁹ and by Dollfus himself^{5,6}. It is important to note that in the published version of his doctoral thesis

which appeared after the book by de Vaucouleurs¹ referred to earlier, Dollfus⁶ states that his "... determination only establishes orders of magnitude" and he assigned no probable error to the value of 90 mb which he derived from his observations.

In 1963, Spinrad, Münch, and Kaplan¹⁰ obtained a spectrum of Mars in the photographic infrared to test for the presence of Doppler shifted water vapor lines. The attempt was successful and led to the additional discovery of three rotational lines in the 5V_3 band of CO_2 ¹¹. The presence of these lines implied a much higher CO_2 abundance in the Martian atmosphere than had previously been assumed. The original observation by Kuiper had been made further in the infrared where the much stronger bands at 1.6μ and 2.06μ were detected. The larger CO_2 abundance of 55 ± 20 m-atm deduced by Kaplan, Münch, and Spinrad¹¹, with the help of laboratory data supplied by Rank et al.¹², implied that a smaller pressure than 90 mb would be adequate to produce the observed intensities of the 1.6μ and 2.06μ bands. The surface pressure derived by these authors was 25 ± 15 mb. The uncertainty was attributed primarily to the error in measuring the extremely weak intensities of the 5V_3 rotational lines on the single plate which had been obtained.

An independent calibration of the Martian 5V_3 lines made by Owen¹³ (from a print of the plate obtained by Kaplan et al.) led to a value of 46 ± 20 m-atm for the CO_2 abundance assuming a Martian atmospheric temperature of 200°K . This is in good agreement with the figure of 50 ± 18 m-atm which

Kaplan, Münch, and Spinrad obtained for this same temperature (the value of 55 m-atm corresponds to a temperature of 230°K). Using this value and Kuiper's¹⁴ new observations of the intensities of the Martian bands at 1.6 μ , Owen and Kuiper¹⁵ derived a surface pressure of 17 ± 9 mb on the basis of direct comparisons with intensities of these same bands observed in the laboratory with a multiple-path absorption tube.

V. Moroz¹⁶ has also observed the 1.6 μ and 2.06 μ CO₂ bands in the Martian spectrum. He used the corresponding telluric bands to get a band strength for the observed intensities and then employed an Elsasser model for the bands to obtain relations between the CO₂ abundance and surface pressure on Mars. Using the abundance derived by Kaplan, Münch, and Spinrad¹¹, Moroz derived a surface pressure of 15^{+15}_{-5} mb.

Most recently, Hanst and Swan¹⁷ have redetermined the absorption intensity of the 5 ν_3 band in the laboratory and obtained results which are very different from those of Rank et al. or Owen. They applied this new value to the measures of the equivalent widths of the lines observed in the spectrum of Mars by Kaplan et al. and derived a CO₂ abundance of 28 ± 13 m-atm ($T_M = 230^\circ\text{K}$). This value was then used in conjunction with one of the three analyses of strong band data presented by Kaplan et al. to derive a surface pressure of 53 ± 29 mb.

Even using the values of Hanst and Swan, the spectrographic results are consistent in suggesting that the pressure is lower than the 85 or 90 mb derived from polarimetric observations. This has led to renewed interest in the role played by particles suspended in the Martian atmosphere. Kuiper¹⁴ has repeated his earlier suggestion that the blue haze particles add to the atmospheric scattering and has suggested that the difference in the Martian albedo between the UV and the visible implies an upper limit to the surface pressure of about 30 mb. This result is in agreement with an independent determination by Musman¹⁸ who derives an upper limit of 27 mb assuming a pure nitrogen atmosphere and no contribution from light reflected from the planet's surface(at 3300 Å).

In this report we have endeavored to re-evaluate the observations and interpretations referred to above. The following section is concerned with the polarimetric observations of Dollfus, the photometric argument of Musman, and the effect of particulate scattering on surface pressure determinations. We have not included a discussion of other photometric pressure determinations since they are less direct and the required assumptions are similar to those which are discussed in Section 2 of this review. The interested reader is referred to de Vaucouleurs¹ and Chamberlain and Hunten¹⁹.

The third part of the report (Section 3) presents a discussion of the results derived from the various spectrographic observations. This is followed by a summary of our

conclusions.

Part II of this report gives details of the calculations and discussions leading to the results presented in Part I.

The general philosophy which has been followed in approaching all of these papers has been to take a detailed look at the work presented by each author without questioning the basic assumptions made, simply to assess the internal errors and uncertainties associated with the results. This has been followed, in the case of the polarimetric observations, with a discussion of the premises on which the work is based. The spectroscopic analysis is founded on principles which are better established and which are consequently not examined in detail. A discussion of these principles can be found in the report by Chamberlain and Hunten¹⁹.

2. POLARIMETRIC AND PHOTOMETRIC DETERMINATIONS OF MARTIAN SURFACE PRESSURE

Introduction

The use of polarimetry in studying the surfaces and atmospheres of the planets was pioneered by B. Lyot², and it was he who in 1929 first published an estimate for the surface pressure on Mars; he obtained a value of 18 mb assuming an atmosphere composed of oxygen and nitrogen. Subsequently, the careful and extensive researches of A. Dollfus raised this figure to 90 mb⁵. During the course of the present reappraisal of the polarimetric measurements, many points of uncertainty arose as to the meaning attached by Dollfus to some of his analytical terms, and to the manner in which he applied his theory to polarimetric observations. In addition it became clear that several of his assumptions were questionable and, since his work was published ten years previously, it seemed fairly certain that he would now hold new views on some of the points in question. One of the authors, therefore, visited Dollfus in Paris (at his invitation), where these matters were discussed. Dollfus was generous with his time, even to the extent of making some measurements in the laboratory on a sample of limonite, in order to resolve one of the difficulties. He

also very kindly produced some of his original data taken in the years 1948 to 1954, so that it was possible to make some calculations to investigate his earlier assumptions^{5,6}.

The result of this visit to Dollfus was a reappraisal of his polarimetric work taking into account the results of his more recent research and the clarifications of his methods. In discussing the application of polarimetry to the deduction of surface pressure, Dollfus emphasized that placing error limits on the result was meaningless; the problem of making such a deduction was insufficiently defined and factors suspected or unknown could give rise to an appreciable, indeterminate error. The findings of this report are consistent with his view. One of the major suspected sources of error is particulate matter in the Mars atmosphere. In this connection, Dollfus stated that he was very careful in the selections he made from observational records. He was able to draw on the results of a continuous photographic patrol of the planet as well as on the polarimetric measurements, and in some years on a photometric patrol. He then selected polarimetric observations which showed no observable deviations that could be attributed to mists or veils (the polarimetric method is very sensitive to such phenomena) and in so doing rejected about 95 percent of the polarimetric observations he had made. Consequently, he concluded that if there was particulate matter present, it was very uniform over the disk and stable over long periods of time.

In examining the original data obtained from Dollfus and the manner in which photometric data was used in the pressure deduction, it became apparent that Dollfus had made an unnecessary assumption in his pressure derivation. Eliminating this assumption resulted in an appreciably lower value for the pressure, but with an increased scatter in his graphical points. Unfortunately this re-analysis was not completed before leaving Paris but Dollfus was sent the details of this work by letter. His reply indicates agreement, and this modified analysis is presented in the sections that follow. This accounts in part for the lower value of the pressure attributed to the polarimetric measurements in this report. Another important factor is the new knowledge concerning the gaseous composition of the Martian atmosphere, which further reduces the derived pressure.

Estimates of the Martian surface pressure have also been made from photometric observation of the ultraviolet albedo of the planet. Because of the very low surface albedo in the ultraviolet, one may assume that the entire Martian brightness is due to Rayleigh scattering from a pure molecular atmosphere and thus obtain an upper limit to the optical thickness and, consequently, the atmospheric pressure. Musman¹⁸ has performed such a calculation and obtained a value which was in closer agreement with spectroscopy than with polarimetry.

The presence of true absorption in the Martian atmosphere is another of the uncertainties that exist in the interpretation of photometric or polarimetric observations. If absorption is appreciable, then both Dollfus' and Musman's derived values of the surface pressure should be raised. Photometric observations of Mars in the past have indicated the presence of absorption as do observations made on the so-called "blue haze" and "blue clearing", but there is no universal agreement on the magnitude of the absorption; Dollfus²¹ believes it to be small.

The determination of pressure by polarimetry falls naturally into two steps, which are treated separately in this section. The first is the deduction from polarimetry, with some input from photometric observations, of the quantity (B_a/B_s). This is the ratio of the brightness of the atmosphere due to sunlight scattered towards the observer on Earth by atmospheric molecules, to the brightness of the ground alone; both evaluated at the sub-Earth point. The second stage is the deduction of the atmospheric pressure from this ratio, using more recent photometric data and further assumptions concerning the composition of the atmosphere. These two sections are preceded by a brief description of the instrumentation and observing errors in polarimetry. There is also a review of Musman's calculation, which is followed by a discussion of the influence of particulate matter in the atmosphere which clearly indicates the importance of a better knowledge of the atmospheric composition.

2.1 Instrumentation*

Before proceeding to the details of the observations and reductions carried out by Dollfus, a critique of his observational methods is in order. Dollfus used a Lyot² polarimeter for the majority of his work. He also designed and built a more sensitive instrument for use with narrow band-pass filters and in other low light level applications. This instrument is described in references 5, 6 and 20 which may be referred to for details of its construction.

Four possible sources of instrumental error were considered. These are:

- a) errors inherent in the polariscope and its use,
- b) errors due to polarization by the Earth's atmosphere,
- c) errors due to parasitic polarization or depolarization introduced by the optical components of the telescope,
- d) errors associated with seeing and scintillation.

From a consideration of effects likely to be introduced by the above errors, it appears that the accuracy of 0.001 which Dollfus ascribes to his observations is reasonable. The accuracy of the polariscope itself is certainly this great. Atmospheric polarization could be a problem when moonlight was present, but Dollfus was aware of this and took precautions to allow for it²¹. Similarly, he was conscious of the effects of parasitic polarization caused by the telescope optics and compensated for this by making comparisons

* The authors would like to express their appreciation to H. T. Betz for his contributions to this section of the report.

between reflecting and refracting instruments²¹. Scintillation will have little effect on polarization measurements of extended objects (e.g., planetary disks) with fairly large telescopes. Poor seeing will lead to poorly defined detail or to blurring of the boundaries of surface features. Since the observatory at which Dollfus made his observations (Pic du Midi) is noted for its excellent seeing, and since the observations were made visually so the image could be inspected at all times, it is doubtful that this was a serious source of error.

One additional consideration involves the question of how carefully the polarization measurements could be made to correspond to a given position on the planetary disk. This is important since Dollfus restricts his observations leading to the pressure determination to the bright areas, and further requires that his "limb" observations be made at an angle of 60° from the sub-Earth point. It appears that the magnification available was adequate for this purpose provided the observations were made in the red and green. This was indeed the wavelength range for the observations referred to.

The final conclusion is that the quality of the observations is strongly dependent on the skill of the observer and his familiarity with the instrument. As indicated above, all exterior factors which could be assessed do not contradict Dollfus' estimate of the observational accuracy achievable by this method.

2.2 The Determination of B_a/B_s from Polarimetry

Dollfus has published the results of his polarimetric determinations of the Martian atmospheric pressure over a period of several years^{3-6,20}. A larger number of observations is included in the more recent papers. Two of these references are practically identical^{5,6}. His Thesis, published in 1955, is exactly reproduced in Suppl. Ann. d'Astrophys. 1957⁶, and the English translation⁵ incorporates a few small improvements made by Dollfus. In the course of his data reduction, Dollfus uses photometric data which, in these publications, he indicated as being unpublished. However such data was located in the literature²² and used in this study; Dollfus later confirmed that this was the data he used²¹.

Theory of the Polarimetric Method

The polarimetric measurements are used to deduce the intensity of radiation scattered by the Martian atmosphere in terms of the intensity scattered by the surface. This ratio is denoted by (B_a/B_s) , the brightness of the atmosphere relative to the brightness of the surface (bright areas only) and is the end product of the polarimetric measurement. In order to obtain this ratio, it is necessary to know the scattering law applicable to the atmosphere and also certain photometric and polarimetric data for the surface. B_s is then found from the measured magnitude of Mars, or from direct photometric measurements. Knowing B_a it is then possible to deduce the amount of gas which causes this scattering, subject to certain restrictions. The pressure

follows from a consideration of the weight of this amount of gas on Mars.

Polarization is defined with reference to the plane containing the source (Sun), scatterer (Mars) and observer (Earth). The radiation is considered in terms of the electric vector components E_{\parallel} and E_{\perp} , parallel and perpendicular to this plane, giving intensities I_{\parallel} and I_{\perp} respectively (see Figure 1). Then the polarization, P , is defined as

$$P = \frac{I_{\perp} - I_{\parallel}}{I_{\perp} + I_{\parallel}} . \quad (1)$$

For a Rayleigh scatterer, I_{\perp} is a constant and

$$I \propto \cos^2 V , \quad (2)$$

so that

$$P = \frac{1 - \cos^2 V}{1 + \cos^2 V} = \frac{\sin^2 V}{1 + \cos^2 V} . \quad (3)$$

In the present case there are two sources of polarized light, the atmosphere P_a , and the ground P_s . These are added arithmetically with weights equal to their respective brightnesses:

$$P = \frac{P_s B_s + P_a B_a}{B_s + B_a} = P_s + \frac{B_a}{B_s} P_a \quad (4)$$

since $B_s \gg B_a$. This procedure is based on the premise that there is no interaction between atmospheric scattered radiation and the surface, or vice versa. In addition, multiple scattering and atmospheric absorption are neglected entirely. From

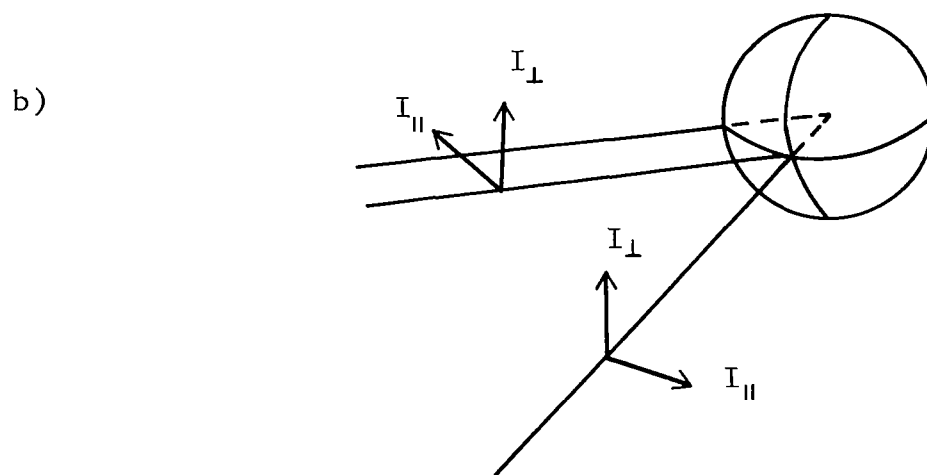
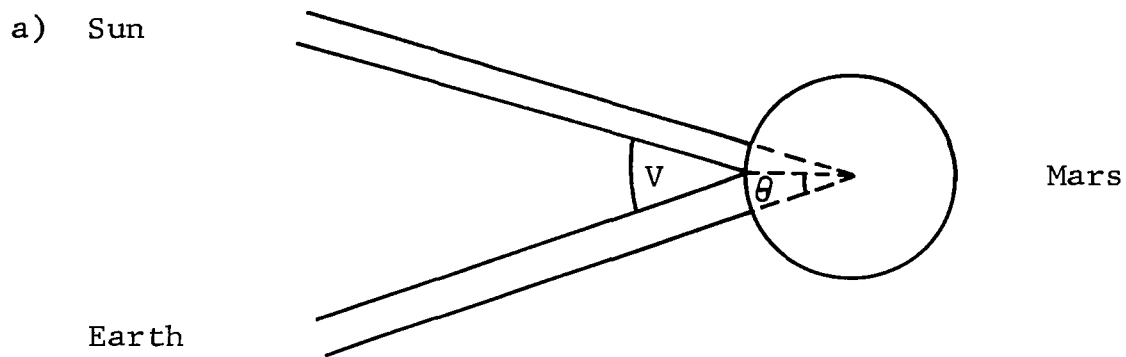


Fig. 1 Diagrams to illustrate the definition of polarization
 a) View perpendicular to plane of vision
 b) $\theta = 0$

recent measurements, Dollfus believes absorption to be small²¹; certainly less than indicated by Öpik²⁵.

It is now convenient to consider the brightness ratio, B_a/B_s at the center of the disk for a particular wavelength λ_o . The above quantities are functions of the phase angle, V , zenith angle θ , and the wavelength, λ . In his earlier publication⁴ Dollfus expressed the surface brightness as

$$B_s \cdot \phi(V) \cdot \psi(\theta) \cdot a(\lambda) .$$

where $a(\lambda)$ is the ratio $B(\lambda)/B(o)$ for $V = \theta = 0$ and $a(\lambda_o) = 1$; B_s is the surface brightness, also for $V = \theta = 0$, $\lambda = \lambda_o$. This separation of variables is clearly a questionable assumption which should be tested, if possible. Later^{5,6,20} Dollfus altered his notation to

$$B_s \cdot \frac{B_V}{B_o} \cdot \frac{B_\theta}{B_o} \cdot a(\lambda) ,$$

where $\frac{B_V}{B_o}$ is the brightness of the ground for phase V , referred to that at zero phase ($V = 0$),

and $\frac{B_\theta}{B_o}$ is the brightness of the ground for the angular distance θ referred to that of the center of the disk ($\theta = 0$).

For the atmosphere,

$$B_a(V) = B_a(0) \cdot \frac{1 + \cos^2 V}{2} .$$

Another convenient approximation is

$$P_s(V, \theta, \lambda) = P_s(V, \lambda) + \Delta(\theta, \lambda) .$$

For material whose polarimetric curve most closely resembles that of Mars, this is a good approximation²³.

Collecting terms one obtains the polarimetric equation for the ground plus atmosphere:

$$P(V, \theta, \lambda) = P_s(V, \lambda) + \Delta(\theta, \lambda) + \frac{B_a}{B_s} \cdot \frac{B_o}{B_v} \cdot \frac{B_o}{B_\theta} \cdot \frac{1}{a(\lambda)} \cdot \frac{\sin^2 V}{2} \sec \theta \cdot \left(\frac{\lambda_o}{\lambda}\right)^4. \quad (5)$$

The dependence of the ratios (B_o/B_v) , (B_o/B_θ) , and $a(\lambda)$ on (V, θ, λ) are discussed below. The factor $(\sec \theta)$ allows for slant paths through the Martian atmosphere. It is shown in Appendix 2.1 that the interpretation of the data is seriously influenced by the assumptions made concerning these ratios.

Determination of B_a/B_s

Dollfus evaluated the polarimetric equation (5) by four different methods which are discussed in more detail in Appendix 2.2, and obtained a value of 0.028 for B_a/B_s . The first method is the most accurate, as Dollfus agrees²¹, and employs measurements made at the center and at the edge of the disk, both at the same wavelength, $\lambda = 0.61\mu$. This method gives a value for B_a/B_s of 0.036 which was considered to be the best value. The last three methods were used primarily as checks. Using the photometric curves which Dollfus²¹ supplied (slightly better than those published), and the original data, a very similar value was obtained. Dollfus' value should be taken as correct since its derivation involves interpolations and

extrapolations of the photometric data.

Dollfus, however, makes the assumption that the surface polarization can be written as the product of two terms, one depending on V only, and the other on θ . This is clearly an approximation, as was also noted by Chamberlain and Hunten¹⁹. It is also an unnecessary assumption, since the photometric data is supplied in a suitable form to avoid this. Recalculation of B_a/B_s without making this assumption reduces Dollfus' value of B_a/B_s from 0.036 to 0.015 but the associated error increases (see Appendix 2.2). The increased scatter is due to uncertainties in the value of θ corresponding to his observations, and in the interpolated photometric curves; the results are very sensitive to the shape of the photometric curves near the terminator of the planet.

The second method considers measurements made at the center of the disk but at two different wavelengths. In this method, Dollfus omitted the wavelength dependence of surface polarization; Dollfus²¹ stated that he was well aware of the approximation, but that at that time there was no data which could be used to allow for this effect. Recent data on limonite, supplied by Dollfus²¹, indicates that the wavelength dependence of the surface polarization may not be very important. Data taken on another sample of limonite by Coulson²⁴, however, shows the effect to be quite significant. The polarization curve for Coulson's sample, on the other hand, does not fit the Mars polarization curve, whereas Dollfus' sample does.

Consequently it was not considered meaningful to use Coulson's data in the recalculation of Dollfus' work.

In the second method, again without separating the θ -V dependence, B_a/B_s falls from Dollfus' value of 0.031 to a value of 0.007; here, there is a large uncertainty, in that the implied polarization at $V = 0$ (from the straight line fitted to the data) is 0.005, instead of zero, (see Appendix 2.2). The reason for this discrepancy is not known.

The third method uses a combination of the first two, and consequently includes the uncertainties of both. In this method, Dollfus made three determinations. The first measurement was towards the limb and the last two towards the terminator. In his calculation there was an arithmetical error, first discovered by Chamberlain and Hunten¹⁹. When this error is corrected, the three determinations yield $B_a/B_s = 0.034, 0.0376$ and 0.0775 respectively. Dollfus notes^{4,5} that the last of these was the least accurate. Recalculation along the lines already indicated reduces these values to $0.050, 0.016, 0.009$ respectively. The fourth method was the least accurate and considered the intensity of light from the whole disk, which would include the occasional cloud. Consequently, this method was not analyzed.

In method three, it is found that the one limb measurement gave a high B_a/B_s (0.050) and the two terminator measurements gave low values (0.016, 0.009). This raises the question as to whether method one gives appreciably different values for

B_a/B_s when using limb or terminator measurements. This question cannot be resolved for lack of data.

In view of the above considerations, it is felt that the best value for B_a/B_s is given by the first method (as revised here) and appears to be 0.015 ± 0.012 (see Appendix 2.3 for a discussion of the meaning attached to the error given). The new value of 0.015 for B_a/B_s is strongly dependent on the way in which errors are assigned to the various quantities. This value is the lowest that can be reasonably accepted (see Appendix 2.2 for further details). The error assigned to B_a/B_s is secondary to the uncertainty in the composition of the atmosphere and the interpretation applied to the polarimetric measurements. Small quantities of aerosols, with their high scattering power, could completely upset the pressure deductions made in this way, as could strong absorption. The effect of absorption in the Martian atmosphere is discussed in more detail in Appendices 2.4 and 2.8, the first of which also contains a brief review of the so-called "blue haze" phenomenon.

2.3 The Determination of Surface Pressure from B_a/B_s

Dollfus'⁵ evaluation of the Martian surface pressure results simply from the calculation of the number of molecules per cm^2 -column in the center of the disk required to produce the observed atmospheric brightness B_a by simple Rayleigh scattering of sunlight. The atmospheric brightness B_a is determined from the ratio B_a/B_s obtained polarimetrically, and from

the total brightness of the disk B_T obtained photometrically. B_T is taken to be equal to the surface brightness B_s because of the high visible surface albedo of Mars. This treatment assumes that the atmosphere of Mars possesses the same scattering and polarizing properties as air.

The surface pressure obtained in this manner is necessarily an approximation since other contributions to B_a such as particulate scattering may lead to significantly different values. In his original work Dollfus⁶ stated that his result was intended only as "an order of magnitude estimate".

On the basis of his original value $B_a/B_s = 0.028$ Dollfus obtained (see Appendix 2.5) an equivalent thickness of 1.9 km for a Martian atmosphere composed of air. This thickness corresponds to a surface pressure of 90 mb. We have repeated Dollfus' calculation using Harris' photometric data²⁸ and obtained a pressure of 117 mb. When the revised value of $B_a/B_s = 0.015$ (see Section 2.2) is used in this calculation, a pressure of 63 mb is obtained.

The problem was reformulated using a slightly different approach (see Appendix 2.5) which made use of the geometric albedo²⁹ of Mars and provided a simpler expression for obtaining the pressure when different molecular compositions were considered. The results obtained with this method were in agreement with our treatment of Dollfus' calculation for an atmosphere of air.

Recent spectroscopic investigations^{11,13} suggest much

larger relative abundances of CO_2 in the Martian atmosphere than in the Earth's atmosphere. The remainder of the Martian atmosphere is assumed to be mainly N_2 . Using the revised value of $B_a/B_s = 0.015$ we obtain the following surface pressures for the atmospheric compositions designated below:

<u>Atmospheric Composition</u>	<u>Martian Surface Pressure</u>
100% air or N_2	63 mb
100% CO_2	42 mb
100% Ar	94 mb
$1/3 \text{ CO}_2 + 2/3 \text{ N}_2$	51 mb

We have not assigned any uncertainty to these values because of the number of problems which are still not yet well defined. Until a better knowledge of the gaseous and particulate content of the Martian atmosphere is available, such assigned uncertainties can only be misleading. What we have hoped to demonstrate is that Dollfus' data (through our revision of B_a/B_s and allowance for increased CO_2 content) lead to lower values for the pressure than 90 mb, and that errors in the photometry as well as the polarimetry must be accounted for in any ultimate assessment of the reliability of this method.

In his calculations, Dollfus did not consider the forward scattering, by the atmosphere, of sunlight reflected from the Martian surface or the scattering by particulate matter suspended in the atmosphere. These problems will be considered briefly in Section 2.5.

2.4 The Determination of Surface Pressure from the Ultraviolet Albedo

If, in the absence of strong absorption, one assumes that the entire ultraviolet brightness of the Martian disk is due to simple molecular Rayleigh scattering of sunlight by the Martian atmosphere, then the optical thickness of atmosphere required to produce this brightness will necessarily be an upper limit as will the corresponding surface pressure. In the ultraviolet, where the surface albedo is very low, the upper limit derived in this manner may be a good estimate of the pressure, providing strong UV absorption in the Martian atmosphere is not prevalent.

Using de Vaucouleurs'³⁰ photometric magnitude of Mars measured at 3300 Å and making the above assumptions, Musman¹⁸ compared the UV reflectivity of Mars with calculated models of a Rayleigh atmosphere and found that an optical thickness of 0.058 at 3300 Å provided the best match.

We have reproduced Musman's technique (see Appendix 2.6) by comparing the ultraviolet reflectivity of Mars with Rayleigh models for a plane atmosphere as calculated by Coulson³¹. Including a correction factor of 2.12 for the sphericity of the Martian atmosphere we obtained results which are in excellent agreement. Coulson²⁴ comments that this correction for sphericity is an oversimplification of the problem because of the optical thickness of the Martian atmosphere in the UV. However, this treatment was only meant to check the results previously

obtained by Musman and is not critical to the conclusions.

The surface pressures listed below are obtained from Musman's calculation extended for additional atmospheric compositions:

<u>Atmospheric Composition</u>	<u>Martian Surface Pressure</u>
100% Air	29.6 mb
100% N ₂	27.0 mb
100% CO ₂	19.0 mb
100% Ar	43.5 mb
1/3 CO ₂ + 2/3 N ₂	21.7 mb

Coulson's calculations also consider planets with various surface albedos. The inclusion of surface reflectivity yields lower values for the optical thickness and surface pressure.

We considered an additional technique (see Appendix 2.6) which employed de Vaucouleurs',²⁹ determinations of the geometric albedo of Mars. This technique yielded surface pressures of 18.5 mb for CO₂ and 26.5 mb for N₂ which serve as an additional check on the above results.

2.5 The Dependence of Pressure Estimates on Atmospheric Properties

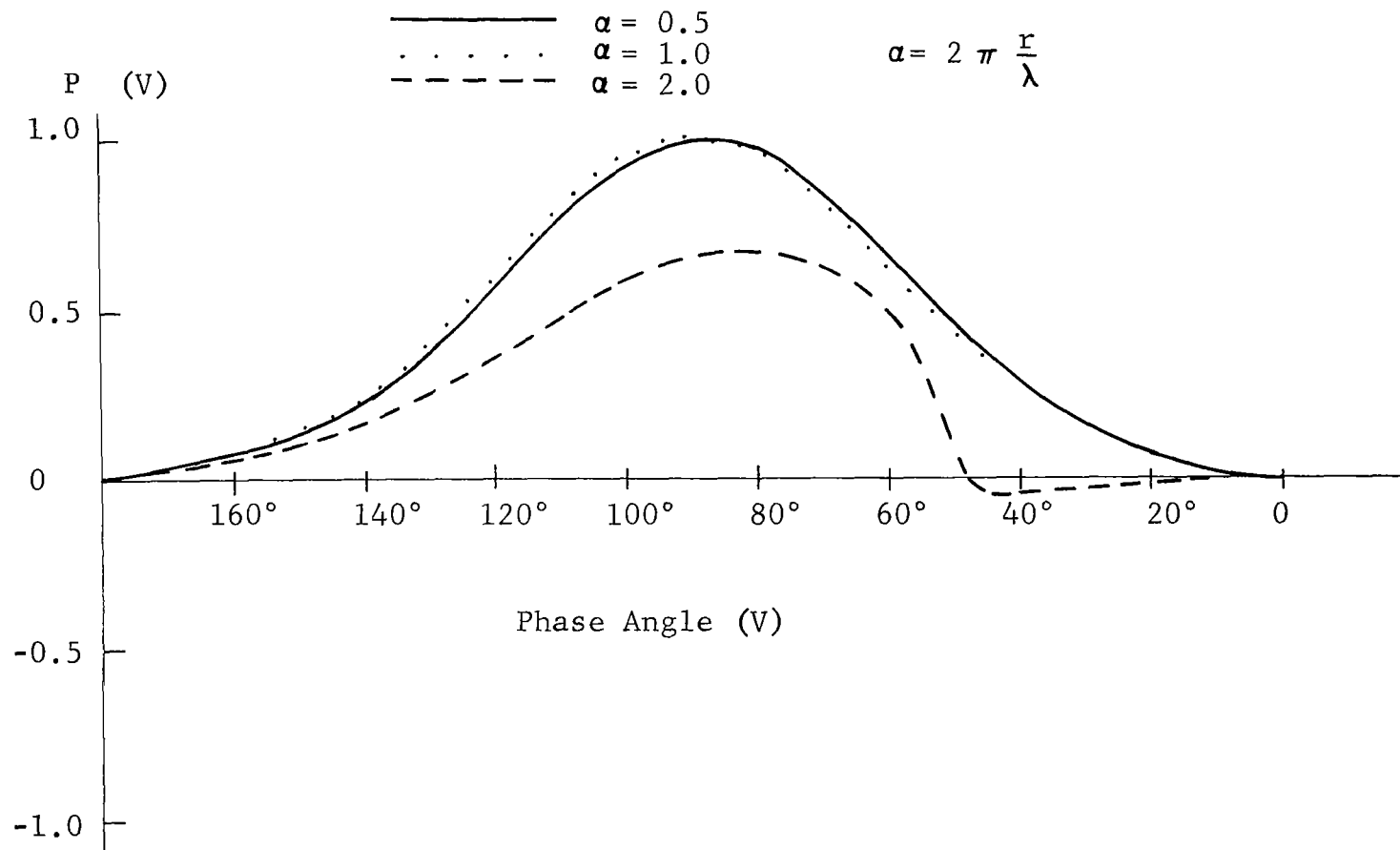
2.5.1 The Effect of Particle Scattering on Visible Pressure Determinations

The determination of Martian surface pressure from Dollfus',⁵ visual polarimetric observations is based on the

assumption that the entire observed atmospheric brightness is due to Rayleigh scattering from a pure molecular atmosphere with polarizing and scattering properties similar to air. These assumptions, while they yield an order of magnitude estimate for the surface pressure, are not realistic. The effect on the surface pressure due to atmospheres of different composition than air has already been considered. The numerous sources which can contribute to the observed brightness of Mars include:

- 1) Rayleigh backscattering from atmospheric gases.
- 2) Rayleigh-type backscatter from very fine particles suspended in the atmosphere.
- 3) Mie backscatter from aerosols.
- 4) Surface reflected or diffused radiation.
- 5) Rayleigh forward scatter of radiation from (4) by atmospheric gases.
- 6) Rayleigh-type forward scatter of radiation from (4) by very fine particles.
- 7) Mie forward scatter of radiation from (4) by aerosols.
- 8) Multiply scattered radiation.

Each of these contribute, not only to the observed brightness but to the observed total polarization. The polarization of sunlight (in the visible) by ice particles of 0.2μ diameter and smaller is shown in Figure 2. Since this polarization is approximately the same as for molecules, then by Eq. (4) (Section 2.2) the brightness of these sources are additive.



Reference 33

Fig. 2 Polarization Function for Particles with Index of Refraction $n = 1.33$ (ice) as a Function of Phase Angle

Thus, for particles in this size range, the contribution to the observed atmospheric brightness can be directly subtracted.

Only the brightness due to (1) should be used in the calculation of surface pressure, but the observed atmospheric brightness may consist of contributions from sources (1), (2), (3), (5), (6), (7), and (8), the last six of which should be subtracted from the observed atmospheric brightness. We have considered the effect of sources (2) and (3) under the above restrictions and find the corrected pressure to be given by the expression (see Appendix 2.7)

$$P \text{ (mb)} = 2.50 \times 10^{-26} \left[\frac{x M_1 + (1-x) M_2}{x \sigma_1^V + (1-x) \sigma_2^V} \right] \left[3.56 - 1.53 \times 10^{-8} \mathcal{N} i_o^V \right],$$

in which:

M_1, M_2 = molecular weights of atmospheric constituents.

σ_1^V, σ_2^V = Rayleigh scattering cross section per molecule for the gaseous constituents in the visible (6200 Å).*

x = fraction of constituent one in the atmosphere.

\mathcal{N} = number of scattering particles per cm^2 -column.

and i_o^V = Mie scattering coefficient for backscatter by particles in the visible = $(i_{\perp} + i_{\parallel})$.

For \mathcal{N} particles per cm^2 -column suspended in an atmosphere composed of $2/3 \text{ N}_2 + 1/3 \text{ CO}_2$ the corrected pressure is given by

$$P \text{ (mb)} = 51 - 2.19 \times 10^{-6} \mathcal{N} i_o^V,$$

* Although Dollfus refers to a wavelength of 6100 Å in his papers, he employed a wavelength of 6200 Å in his calculations as in his work on the planet Mercury. Because of the wide bandwidths of the filters employed, this difference is not felt to be significant, and the calculations in this report consider the value of 6200 Å.

which is simply the pressure calculated in the absence of particles with a correction term for particulates. For 0.2μ diameter ice particles, Penndorf³² gives the Mie scattering coefficient as $i_o^V \sim 0.020$. Thus, only $N \sim 7.1 \times 10^8$ such particles per cm^2 -column would be required to reduce the pressure to 20 mb which is in rough agreement with the spectroscopically determined values.*

The contribution from sources (5), (6) and (7) above may also be significant in the visible where the surface albedo is 60%. Qualitative arguments show that both for Lambertian or lunar-type surface scattering laws, the inclusion of this effect would probably reduce B_a/B_s somewhat (rather more for the Lambertian surface).

Atmospheric absorption in the visible will also affect the brightness and hence the pressure estimate. The consequence of absorption on Dollfus' results is discussed briefly in Appendix 2.8.

2.5.2 The Effect of Particle Scattering on Ultraviolet Pressure Determinations

In our earlier discussion of Musman's work¹⁸, we calculated the Martian surface pressure under the assumption that the entire brightness of Mars was due to Rayleigh scattering by a pure molecular atmosphere (also assuming no strong absorption). In order to consider the effect on the pressure of

* The mean concentration of Aitken nuclei (particles in the range 0.005μ to 0.2μ) in the Earth's atmosphere is $1.5 \times 10^5 \text{ cm}^{-3}$. Thus a 50 m column would provide the necessary concentration.

\mathcal{N} scattering particles per cm^2 -column in the Martian atmosphere, we must subtract the brightness due to particle scattering from the observed atmospheric brightness. This subtraction yields the actual molecular Rayleigh scattered brightness which is used in the pressure calculation. Performing this subtraction (see Appendix 2.9) we find the corrected surface pressure to be given by

$$P \text{ (mb)} = 1.18 \times 10^{-26} \left[\frac{x M_1 + (1-x) M_2}{x \sigma_1^b + (1-x) \sigma_2^b} \right] \left[4.5 - 9.18 \times 10^{-9} \mathcal{N} i_o^b \right],$$

where

M_1, M_2 = molecular weights of atmospheric constituents

σ_1^b, σ_2^b = Rayleigh scattering cross section per molecule for the gaseous constituents in the ultraviolet (3300 Å).

x = fraction of constituent one in the atmosphere.

\mathcal{N} = number of scattering particles per cm^2 -column.

i_o^b = Mie scattering coefficient for backscatter by particles in the ultraviolet = $(i_{\perp} + i_{\parallel})$.

For \mathcal{N} particles per cm^2 -column suspended in an atmosphere composed of $2/3 \text{ N}_2 + 1/3 \text{ CO}_2$, the surface pressure is given by

$$P \text{ (mb)} = \left[22.2 - 4.53 \times 10^{-8} \mathcal{N} i_o^b \right].$$

For 0.2μ diameter ice particles, Penndorf³² gives the Mie scattering coefficient as $i_o^b \sim 0.151$. The presence of $\mathcal{N} \sim 7.1 \times 10^8$ ice particles of 0.2μ diameter, which reduced

the visible determination to 20 mb, will reduce the pressure obtained from the UV albedo to 17.3 mb which is in reasonable agreement.

2.5.3 The Agreement of Visible and Ultraviolet Pressure Determinations

We have shown that consideration of the presence of scattering particles in the Martian atmosphere will yield lower estimates of the surface pressure than those obtained assuming only Rayleigh scattering by a pure molecular atmosphere. For an atmosphere composed of $2/3 \text{ N}_2 + 1/3 \text{ CO}_2$ with \mathcal{N} scattering particles per cm^2 -column in suspension, the visible determination was given as (Section 2.5.2)

$$P_V \text{ (mb)} = 51 - 2.19 \times 10^{-6} \mathcal{N} i_o^V ,$$

while the ultraviolet determination was (section 2.5.3)

$$P_b \text{ (mb)} = 22.2 - 4.53 \times 10^{-8} \mathcal{N} i_o^b .$$

In both cases, the results are simply the pure molecular estimates reduced by a correction term which compensates for that portion of the brightness due to scattering by particles. Both expressions can be equated since the pressure is certainly independent of the wavelength of observation. Furthermore, if only one particle size and type is assumed present, we can solve for \mathcal{N} and obtain the number of particles which will bring the visible and ultraviolet results into harmony.

This value is given by (see Appendix 2.10)

$$N = \frac{2.88 \times 10^7}{2.19 i_o^V - 0.0453 i_o^b} \frac{\text{particles}}{\text{cm}^2\text{-column}}.$$

Substituting this result into the pressure expression gives
(see Appendix 2.10)

$$P_{V,b} \text{ (mb)} = 51 - \left[\frac{63}{2.19 - 0.0453 \frac{i_o^b}{i_o^V}} \right]$$

Figure 3 presents a smoothed version of Penndorf's³² curve for ice particles giving $i_o(\alpha)$ for backscatter versus α ; where $\alpha = 2\pi \frac{r}{\lambda}$ is the size parameter. Over the restricted range of interest this can be approximated by

$$\log i_o(\alpha) \cong 3.22 \log \alpha - 1.72.$$

Thus, the ratio i_o^b/i_o^V is given as

$$\frac{i_o^b}{i_o^V} \cong \left(\frac{\lambda_V}{\lambda_b} \right)^{3.22} \cong \left(\frac{.62}{.33} \right)^{3.22} \cong 7.64$$

independent of particle size. The surface pressure,

$$P_{V,b} \text{ (mb)} = 51 - 34.2 = 16.8 \text{ mb},$$

is then compatible with both the visible and UV observations.

The fact that this ratio i_o^b/i_o^V is approximately constant suggests that the same compatible pressure of 16.8 mb exists for all particle sizes (less than 0.2μ dia for ice)

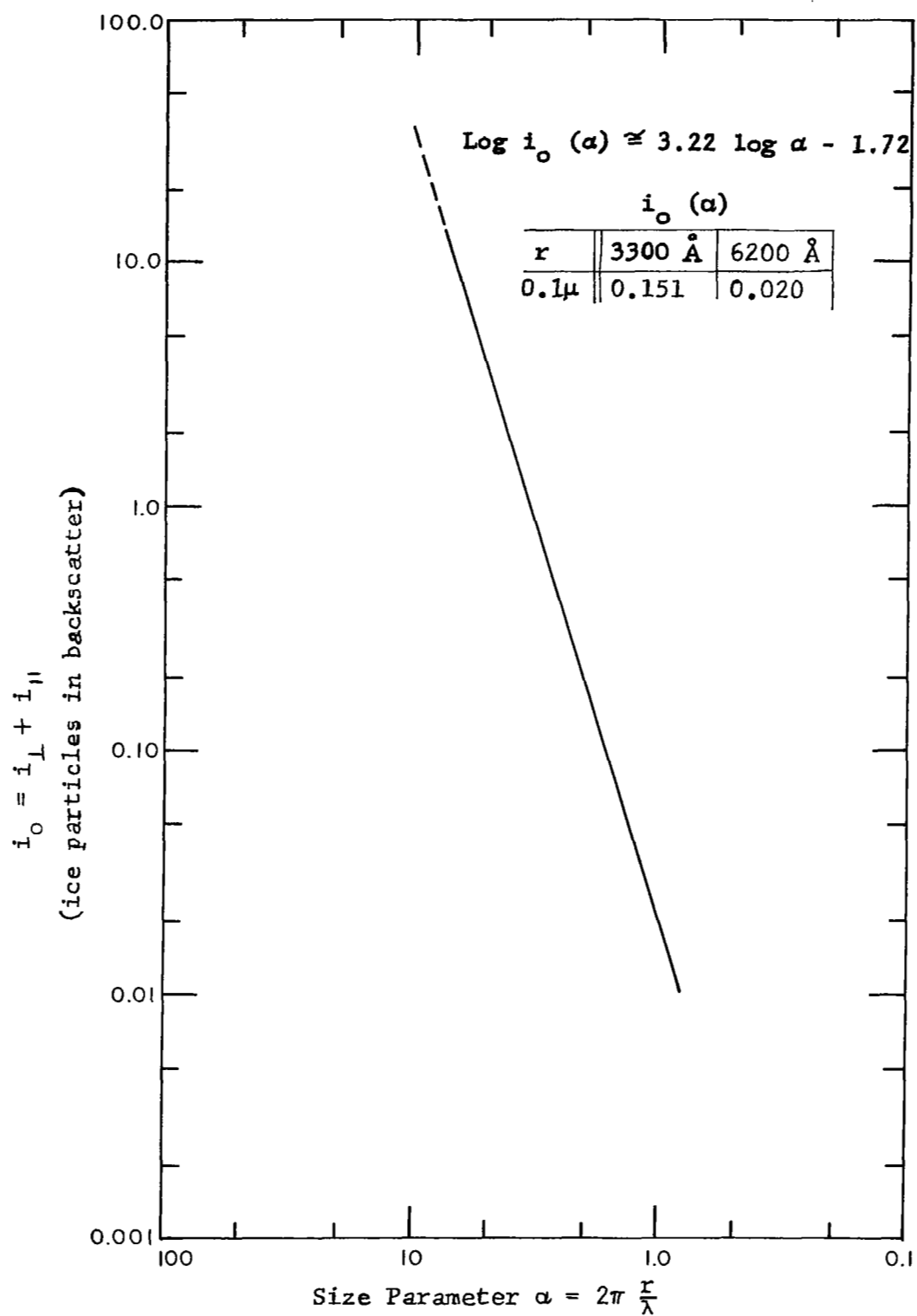


Fig. 3 Mean Mie Scattering Coefficient for Backscatter due to Ice Particles

and therefore for any distribution of particle sizes in this range although the number of particles required for compatibility varies. For 0.2μ diameter ice particles we require $N^p = 7.8 \times 10^8$ per cm^2 -column to bring the visible and ultraviolet determinations into accord. Consideration of larger particles does not yield such simple results.

2.6 Conclusions

The methods for deducing the Martian surface pressure from polarimetry have been analyzed in detail. The first stage in this deduction was the determination of the ratio B_a/B_s from the polarimetric observations of the Martian disk. In considering the four methods Dollfus used for determining B_a/B_s it is evident that only the first should be considered seriously, as the uncertainties in the other three are much greater. Dollfus²¹ has expressed agreement with this evaluation. The large scatter in the final graphical plot from which B_a/B_s was obtained (see Appendix 2.2) was probably due to several factors, but at least two were apparent as major contributors. One was the inadequate photometric data available for relating the brightness of the ground between various parts of the disk, consequently requiring very uncertain extrapolations and interpolations. The other was the uncertainty in the zenith angle θ , at which the observations were made; this applied especially to observations made towards the terminator. More data taken with regard to these two questions should reduce the error in B_a/B_s estimated from the data.

The analytical method used by Dollfus to obtain the B_a/B_s ratio makes the assumption that the surface brightness can be expressed as the product of three functions of the single variables V , θ and λ respectively. It is not clear why Dollfus made this apparently unnecessary assumption which has the effect of raising B_a/B_s , although it does improve the apparent precision of the results. We have revised Dollfus' calculation by not separating the θ - V dependence. An account of the revised calculations was sent to Dollfus to which he replied that, considering the discussions held with him at Meudon, he thought the new pressure determination was essentially correct.

Using more recent photometric data by Harris and taking the Martian atmosphere to consist of $1/3$ CO_2 and $2/3$ N_2 (as a somewhat extreme model for the spectroscopic results) gave a further reduction in surface pressure. The result of these two factors, a reduction in B_a/B_s and a larger CO_2 content, is to bring the polarimetric and spectroscopic determination into agreement within experimental error. No such error is quoted for the polarimetric results because we feel it would be misleading. An error is given (see Appendix 2.3) for the deduced value of B_a/B_s , determined by considering the scatter in data points and uncertainties in extrapolation of photometric data. Consequently the error in the pressure determination is at least as great as this and probably very much greater. The uncertainties are due to at least three factors: inadequate

knowledge of the properties of the Martian surface, atmospheric scattering properties and atmospheric absorption.

Some calculations were made to investigate the influence of particles in the Martian atmosphere. These showed that very small number densities were sufficient to appreciably reduce the value for the surface pressure. For ice particles having diameters of 0.2μ , for example, it was found that only about 7.8×10^8 particles per cm^2 -column were required to reduce the estimates obtained in the visible and ultraviolet regions of the spectrum to a common value of 16.8 mb, which is in reasonable agreement with current spectroscopic values. We do not wish to suggest that this agreement proves that the deduced number and size distribution of particles is actually present in the Martian atmosphere. The calculation is simply meant to indicate two things: a) that the presence of fine particles (which would not be detected polarimetrically) leads to an overestimate of the surface pressure if not accounted for, and b) that it is possible to make the pressure determinations based on the UV albedo and the visual polarimetry mutually compatible and compatible with the spectroscopic results using a very simple particle configuration.

Clearly several different particle size distributions, compositions and concentrations could be imagined which would lead to similar results. It is our present lack of knowledge about the particulate content of the Martian atmosphere which

makes surface pressure determinations based on polarimetric and photometric observations so indeterminate at this time.

3. SPECTROSCOPIC DETERMINATIONS OF SURFACE PRESSURE

3.1 Martian CO₂ Abundance

Three determinations^{11,13,17} of the Martian CO₂ abundance have been made by comparing laboratory absorption measurements of the $5\frac{1}{3}$ CO₂ bands with equivalent widths obtained from a Martian spectrogram¹¹. These calculations of CO₂ abundance are independent only as far as the laboratory calibration is concerned; all three depend on one spectrograph plate to provide the Martian CO₂ absorption. Both Kaplan, Münch, and Spinrad, (KMS) and Hanst and Swan used the equivalent width given by (KMS) for the Martian rotational lines, and obtained a CO₂ abundance by comparison with integrated absorptions for these lines deduced from laboratory measurements. The KMS paper relies on the integrated absorption provided by Rank et al.¹², while Hanst and Swan provided independent absorption measurements of the $5\frac{1}{3}$ CO₂ band. Owen* obtained laboratory spectra for a range of pressures and optical densities, and from a comparison with the Martian spectra estimated upper and lower limits for the Martian CO₂ abundance. The results of these three determinations of Martian CO₂ abundance, as presented by the authors, are given in Table I.

* In order to insure an objective approach, Mr. Owen did not participate in the review of the papers on this subject of which he was a contributing author.

Table I

THE MARTIAN CO₂ ABUNDANCE

<u>Author</u>	<u>CO₂ Abundance at 200°K (m-atm)</u>
KMS	50 ± 18
Owen	46 ± 20
Hanst and Swan	27 ± 12 (with the m-atm defined for 300°K)

The KMS determination of the Martian CO₂ abundance can be discussed on the assumption that the absorption for the J = 8, 10 and 12 lines in the R branch of the 5 ν_3 CO₂ band in the Martian spectrum can be described by the weak line approximation³⁴. The equivalent width of a weak absorption line is equal to the product of line strength times the optical density of the absorbing gas, i.e., $W = Su$, where W is the equivalent width, S is the rotational line intensity, and u is the CO₂ optical density. The optical density can be expressed as the product of the amount of gas (w) along the vertical path times the effective air mass (η). An average equivalent width of $5 \times 10^{-3} \text{ cm}^{-1}$ was determined for the R branch J = 8, 10 and 12 lines of the Martian 5 ν_3 CO₂ band. Using Rank's data, adjusted slightly to fit a Boltzmann distribution³⁵, KMS estimated an intensity of $6.3 \times 10^{-6} \text{ cm}^{-1}$ per cm-atm NTP for the entire 5 ν_3 band.

The Martian CO₂ abundance obtained from the infrared observations is dependent on the effective Martian temperature

which is somewhat uncertain. In (KMS) the abundance was presented for temperatures of 230°K and 200°K, with 230°K apparently the preferred value. If recently published Martian model atmospheres^{37,38} are used to estimate the effective temperature, it appears that a temperature of 230°K is probably high. On the basis of these models (Figure 4), it is estimated that the temperature corresponding to the effective broadening pressure is between 180°K and 220°K. In our analysis the abundance for an assumed Martian temperature of 200°K is emphasized, and variation of abundance for temperatures in the range 150°K to 250°K is considered.

Since the KMS paper was published, a small correction has been made in the air mass³⁹ which increases its value from $\eta = 3.6$ to $\eta = 3.9$, and thus reduces the CO₂ abundance by about 10 percent.

A small correction should also be considered to account for the possibility of rotational lines in the part of the R branch returning from the band head overlapping with the rotational lines used for the abundance calculation. The wavelengths of the rotational lines for these higher J values ($J \approx 40$) are apparently not reported in the literature, and accurate calculations of the positions of these lines cannot be performed because the rotational constant (D) is not known. If the positions are calculated with the expression⁴⁰

$$\nu = \nu_0 + 2 B' + (3B' - B'') J + (B' - B'') J^2, \quad (1)$$

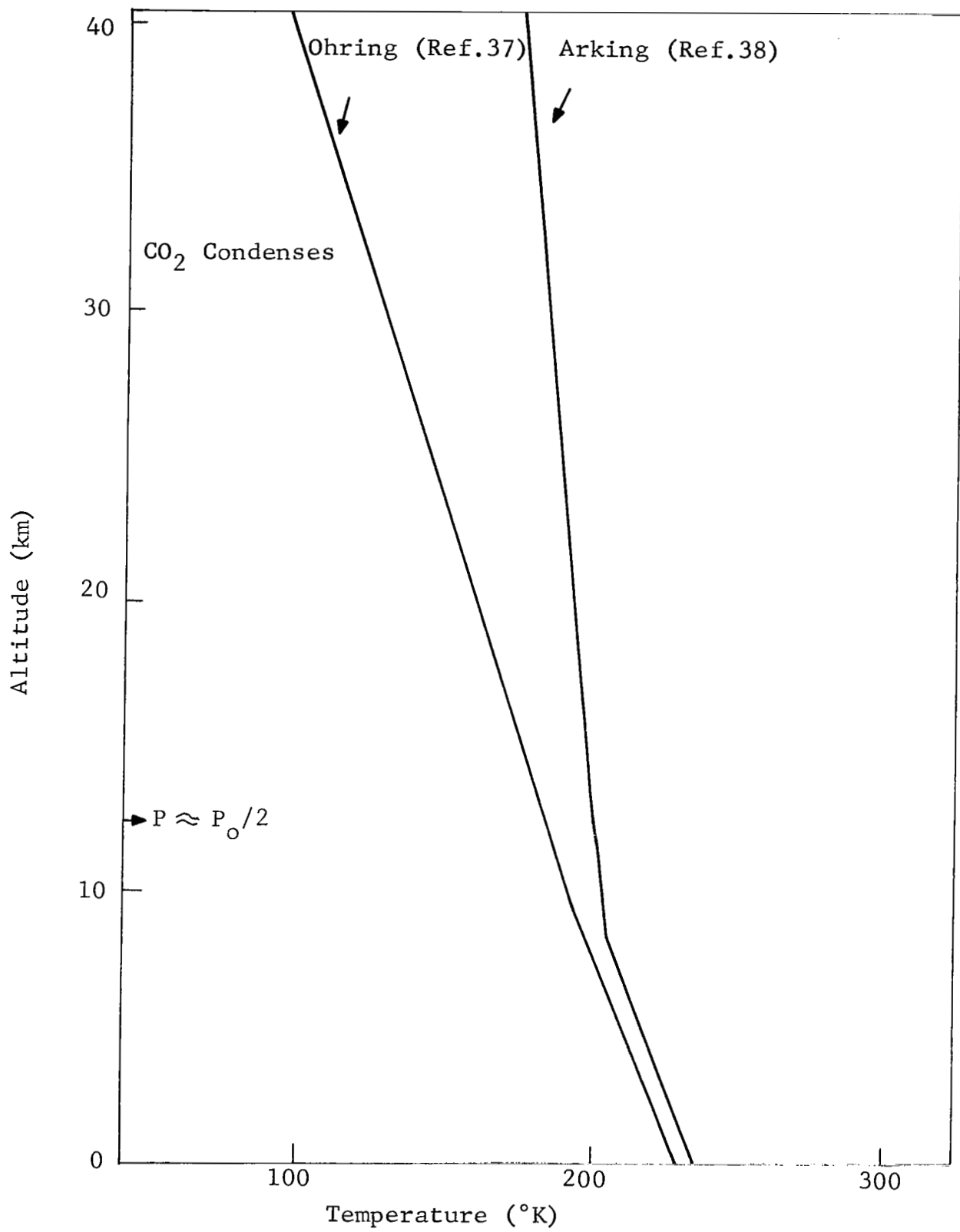


Fig. 4 Martian Atmospheric Temperature Distribution

it is found that the $J = 8, 10$ and 12 lines are overlapped by the $J = 40, 38$ and 36 lines, respectively. The rotational line intensity used by KMS was the average intensity of the lines for $J = 8, 10$ and 12 , i.e.,

$$S = \sum_{J=8,10,12} S_J/3 . \quad (2)$$

If overlapping does occur, this "line intensity" should include the average intensity for the $J = 36, 38$ and 40 lines, or

$$S = \sum_{J=(8,36)(10,38)(12,40)} S_J/3 . \quad (3)$$

At a temperature of 200°K , the effect of overlapping increases the value of S by eight percent, and reduces the CO_2 abundance by a corresponding amount. Both Kaplan³⁵ and Rank⁷⁴ have stated that Rank's laboratory data indicated no overlapping of the $J = 8, 10$ and 12 lines. Hence this correction should be considered more as an uncertainty until these data are made available.

To summarize, the analysis of the CO_2 abundance obtained with the weak line approximation suggests the following three corrections to the value given by (KMS), all of which tend to reduce the amount of CO_2 on Mars:

- 1) The air mass is $\eta = 3.9$ rather than 3.6 ;
- 2) The best estimate of the effective Martian temperature is considered to be 200°K rather than 230°K ; and
- 3) The lines for $J = 8, 10$ and 12 are assumed to be overlapped with higher J value rotational lines.

Based on these corrections it is suggested that $w = 40$ m-atm is a more realistic estimate for the weak line approximation. The effect of a small amount of saturation, (see Appendix 3.1) is to increase this value by 7.5 percent, yielding a CO_2 abundance of 43 m-atm at 200°K.

The uncertainty that should be associated with this abundance was evaluated by calculating the relative error⁴⁴. The details of the method and the relative errors used for each component in the equation are described in Appendix 3.2. It should be emphasized that the relative errors used in the calculation were taken as upper and lower limits, so the final values of uncertainty indicate the extreme limits of the abundance rather than a probable error. The result of this analysis yields an abundance of 43 ± 25 m-atm.

Owen measured absorption spectra of the $5\mu_3$ CO_2 bands for optical densities from 85 to 350 m-atm, and found that the laboratory path lengths of 241 ± 44 m-atm (at $T = 297^\circ\text{K}$) provide absorption intensities comparable to the Martian absorption intensity. Owen was able to use the corrected value of the air mass (3.9) to convert this CO_2 optical density to a vertical-path Martian CO_2 abundance at 300°K. The Boltzmann distribution was then applied to account for the temperature dependence of rotational line intensity, and the resulting value was multiplied by (273/297) to provide an abundance that corresponds to standard temperature. Owen included the effect on the abundance of overlapping rotational lines in the R branch; and, although he

considered the overlapping of lines for $J = 10$ and $J = 40$, the abundance would be altered by only two percent from his value if the $J = 10$ and 38 lines overlap. As mentioned above, this should probably be considered an additional uncertainty in the final result, the only question being whether or not the correction for overlapping should be included in the adopted value. The CO_2 abundance determined in this manner is given as 46 ± 15 m-atm at 200°K and 51 ± 17 m-atm at 230°K . Owen has not accounted for the effect of a small amount of saturation, which would tend to increase the value of the CO_2 abundance.

Hanst and Swan measured the absorption intensity of the (unresolved) R branch of the 5v_3 band in the laboratory. Their maximum path length was about 400 m-atm leading to a maximum absorptivity slightly greater than 5% at the band head. Using the weak-line approximation they derived the following values for the band intensity:

$$S = 0.0480 \text{ cm}^{-1}/\text{km-atm} \quad (300^\circ\text{K}) \quad T_M = 230^\circ\text{K},$$

$$S = 0.0514 \text{ cm}^{-1}/\text{km-atm} \quad (300^\circ\text{K}) \quad T_M = 200^\circ\text{K},$$

where T_M denotes the assumed mean temperature for the Martian atmosphere.

We have corrected these intensities by reducing the km-atm to NTP so they can be compared with the other values discussed in this report. We then obtain for the Martian CO_2 abundance

$$w = 23 \text{ m-atm (NTP)} \quad T_M = 230^\circ\text{K}$$

$$w = 21 \text{ m-atm (NTP)} \quad T_M = 200^\circ\text{K}$$

Evaluating the uncertainties associated with this work in the same manner as in the preceding two cases, and again choosing $T_M = 200^\circ\text{K}$, we find $w = 21 \pm 18$ m-atm (see Appendix 3.2).

The Martian CO_2 abundance determinations offered by KMS and by Owen are in excellent agreement considering the uncertainty of both measurements. After correcting for the effects of saturation and the overlapping of rotational lines the KMS abundance is $43 (\pm 25)$ m-atm compared to Owen's value of $46 (\pm 20)$ m-atm. The CO_2 abundance is a function of temperature through the temperature dependence of the rotational line intensity, and up to this point no contribution to the error has been included to account for the temperature uncertainty. The CO_2 abundance from both KMS and Owen is plotted vs. effective Martian temperature in Figure 5. The information presently available suggests that the effective Martian temperature is probably between 180°K and 220°K . If an average temperature of 200°K is used, the uncertainty in the abundance should be increased by about ± 3 m-atm to account for this temperature range. From this analysis it would appear that the best value of CO_2 abundance to use in the pressure calculation is 45 ± 25 m-atm.

In making this judgment, we are excluding the work of Hanst and Swan. This step is necessarily somewhat arbitrary since we have not found any errors in the Hanst and Swan paper which would account for the large discrepancy between their value of the abundance and those derived by KMS and Owen. Chamberlain and Hunten⁷⁵ have suggested that "if anything," a

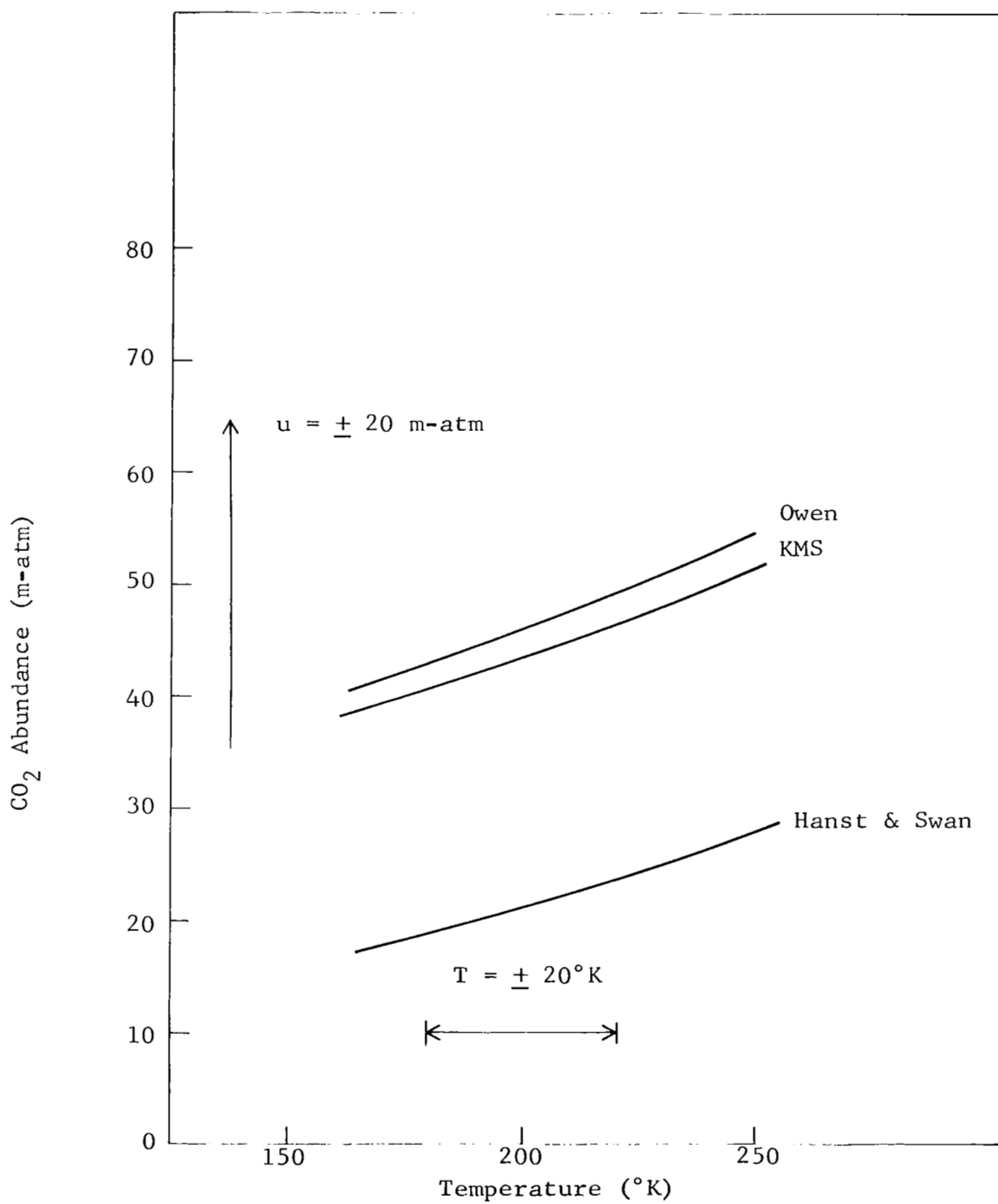


Fig. 5 CO₂ Abundance on Mars vs. Effective Martian Atmospheric Temperature

lower weight should be assigned to the AVCO results because of the very small amount of absorption available for measurement. In addition, preliminary results obtained by Inn⁷⁶ using a resolution similar to that of Hanst and Swan appear to agree with the Rank calibration. Inn stressed the point that he felt a high resolution study would be required before he would be confident of the reliability of his determination, but at the present time, available evidence appears to favor the lower values of absorption intensity. (See note p. 76.)

The CO₂ abundance calculations of both KMS and Owen are very straightforward, and utilize well known and accepted expressions requiring a minimum of subjective interpretation. It is believed that no large error is introduced in the computational procedure. Therefore, if the abundance given is in error, it is probable that this error is associated with the basic data used in the calculations. In the KMS calculation such an error must be introduced by; the equivalent width, the intensities given by Rank, or in the use of Rank's intensities; while in Owen's work, the equivalent width and his own laboratory investigation are involved. The determination of the equivalent width is of course a very inaccurate measurement, but a large uncertainty is already attached to this value. The fact that only one observation of the Martian spectrum was available is the largest barrier to an expression of confidence in the equivalent width measurements. The laboratory calibrations are

more reliable, but the work of Hanst and Swan indicates that a more extensive investigation of the $5\mu_3$ absorption intensities is required.

3.2 The Determination of the Martian Surface Pressure

3.2.1 Introduction

The Martian surface pressure has been determined from infrared absorption measurements by KMS¹¹, by Owen and Kuiper¹⁵ (hereafter referred to as (OK)), and by Moroz¹⁶. The basis for this pressure determination is the fact that, except for weak lines, the infrared absorption depends on both the total gas pressure and the CO₂ optical density. Since the CO₂ abundance is known from measurements of the weak line absorption of the $5\mu_3$ CO₂ band, the strong line absorption can be reduced to a function of pressure alone. KMS used available measurements of absorption for the strong CO₂ bands near 2μ and calculated the pressure from (a) the exponential law for absorption and (b) the band model for strong absorption lines. In the work of (OK), equivalent widths were obtained for the 1.6μ CO₂ bands over a range of pressures and optical densities, and the pressure was deduced by a comparison of this data with the observed Martian equivalent width. Moroz applied an Elsasser band model to determine the relation between optical density and pressure from his observations of the 1.6μ and 2μ CO₂ bands, adopting the abundance given by KMS to solve for the surface

pressure. As their final result, Kaplan, Münch and Spinrad gave a Martian surface pressure of 25 ± 15 mb, Owen and Kuiper gave a pressure of 17 ± 9 mb (± 3 prob. error), and Moroz gave a pressure of 15^{+15}_{-5} mb.

3.2.2 The Pressure Derivation of Kaplan, Münch and Spinrad¹¹

In the KMS paper, three different calculations of the Martian pressure were presented which were based on (a) Sinton's⁴⁵ measurements of Martian absorption at 2μ , (b) Kuiper's observations of Martian absorption at 2μ ⁴⁶, and (c) Kuiper's equivalent width for Martian and Martian plus telluric absorption at 2μ . The pressure calculations in the first two methods are obtained by finding conditions for which the strong CO₂ line absorption on Mars is equal to a known absorption in either (1) the Earth's atmosphere, or (2) a laboratory experiment. The absorption is described by an expression of the form

$$A = \int_{\Delta\nu} (1 - e^{-k_\nu u}) d\nu ,$$

where k_ν is the absorption coefficient, u is the optical density, and ν is the wave number. When the two absorptions are equal, the components are also, and since the optical density is known from the CO₂ abundance and the geometry of the observation, the pressure can be calculated if the pressure dependence of the absorption coefficient is known.

KMS used the absorption coefficient for a series of pressure-broadened non-overlapping rotational lines that are completely saturated out to several Doppler widths, which appears to be a reasonably accurate description of the physical situation⁸. When absorption by the entire band is considered, the temperature dependence of the Boltzmann factor ($e^{-E/kT}$) that accounts for the distribution of population in various rotational levels is eliminated by integrating over the band.

Sinton⁴⁵ observed that the Martian absorption at the center of the 2μ bands is equivalent to an increase of 1.86 air masses for the Earth's atmosphere, so the effective Martian pressure can be determined by letting $k_1 u_1 = 1.86 k_2 u_2$ (where the subscripts (1) and (2) refer to the Earth and Mars, respectively).

The estimate of the Martian pressure made with Kuiper's 2μ CO_2 laboratory and Martian absorption measurements was accomplished in a similar manner, by determining laboratory conditions for which the products of absorption coefficient times optical density should be equal for the laboratory conditions and on Mars.

A third estimate of the pressure was made using equivalent widths of the 2μ CO_2 bands obtained from Kuiper's data. It was assumed that these equivalent widths can be represented by the strong line approximation so that the Martian pressure is given by

$$P_1 = \frac{P_2 u_2}{u_1} \left(\frac{W_{12}^2 - W_2^2}{W_2^2} \right) \left(\frac{T_1}{T_2} \right)^{1/2} \begin{pmatrix} 1 = \text{Mars} \\ 2 = \text{Earth} \end{pmatrix} .$$

Our review of these pressure calculations reveals no serious disagreement with either the methods or the assumptions of KMS. The final values of pressure given in this report therefore differ from theirs only because of the change in the abundance estimate described above.

The uncertainty associated with these pressure determinations has been calculated in the same way as those for the CO₂ abundance, i.e., upper and lower limits were determined by adding the relative errors for those parameters involved in the computation. The details of the error calculations are given in Appendix 3.3. The largest uncertainty in the pressure calculation is that associated with the abundance; since the abundance enters directly into the pressure in all three calculations, the relative errors for the pressure are in all cases larger than that of the abundance. While the effect of CO₂ self-broadening enters into all the calculations, only the pressure determined from Kuiper's 2μ CO₂ laboratory absorption measurements is directly dependent on the self-broadening factor. An uncertainty in the pressure determined with Martian and telluric equivalent widths of the 2μ CO₂ bands that cannot be completely evaluated is the assumption that these equivalent widths can be represented by the strong line approximation. Although it is stated that this is evident from the data of Howard, Burch,

and Williams⁴⁷, both values of equivalent width are in fact outside the range of this data, and it is not certain either that (a) these equivalent widths are proportional to $(p_u)^{1/2}$, or (b) that both have the same dependence on p_u . From their position on the curve of growth it appears that, if the square root approximation is not a valid representation of the equivalent widths, these values will still be proportional to the square root of pressure, but proportional to a higher power of the optical density. If this were the case, the dependence of the telluric equivalent width would probably be equal to or greater than that of the Martian lines, and if greater, the Martian pressure would be larger than given here. It is not possible to evaluate this uncertainty without additional laboratory observations of the 2.06μ band equivalent widths as a function of pressure and optical density.

The results of the revised pressure calculations are summarized in Table II.

Table II

REVISED PRESSURE CALCULATIONS

<u>Strong Band Data</u>	<u>Pressure (mb)</u>
Sinton's 2μ band data	34 ± 30
Kuiper's 2μ band lab comparison	36 ± 31
Kuiper's 2μ band equivalent widths	30 ± 29

From our review of the KMS Martian pressure calculations it is concluded that the best estimate of the pressure that can be made with their data is 33 ± 30 mb rather than 25 ± 15 mb. The pressure given here is higher than that of KMS because (a) a correction has been made for an apparently erroneous value of air mass, (b) it is believed that the temperature of 230°K used by KMS is approximately 30°K higher than warranted by presently available information, and (c) the effect of overlapping rotational lines was apparently not included by KMS. Thus the increase in pressure is due to the decrease in CO₂ abundance that results from the consideration of these three factors.

3.2.3 The Pressure Derivation of Owen and Kuiper

Owen and Kuiper¹⁵ determined the Martian surface pressure using the 1.6μ CO₂ bands, for which the average equivalent width of the Martian bands is 15.8 Å¹⁴. Equivalent widths of the 1.6μ CO₂ bands were determined in the laboratory over a range of pressures and optical densities for gas mixtures of 100% CO₂, 10% CO₂-90% N₂, and 25% CO₂-75% N₂, and plotted vs. pressure for each optical density. In principle the effective Martian pressure can be obtained from the intersection of the line representing the Martian equivalent width with the curve for the equivalent width determined in the laboratory that corresponds to the Martian CO₂ abundance. However, a completely empirical determination is not possible because the path lengths

available in the laboratory are only about 10 percent of those required to simulate the Martian conditions. The intercept of the line representing the Martian equivalent width with an extrapolated curve intended to represent the Martian abundance was determined for the three gas mixtures used and the resulting pressures were compared with the computed weight of an atmospheric column of this gas on Mars. The Martian surface pressure, determined from the intersection of a plot of measured pressure vs. calculated pressure with a straight line of unit slope, was 17 ± 9 mb (± 3 prob. error).

The critical point in the (OK) pressure determination is their extrapolation to optical densities corresponding to the Martian atmosphere. The equivalent width data has been examined in an effort to determine what extrapolation might be justified, and to provide an estimate of the uncertainty associated with this extrapolation. The dependence of equivalent width on optical density and pressure was determined on the assumption that the equivalent widths can be expressed by the relation

$$W = C p^{1/a} u^{1/b}$$

and the constants a and b were determined by the method of least squares. In Figs. 6 and 7 the values of b and the $\Delta \log W$ that would result from doubling the amount of gas are plotted vs. the logarithmic pressure; a similar plot of a vs. the logarithm of optical density is shown in Figure 8. The corresponding values for the square root approximation are $a = b = 2$

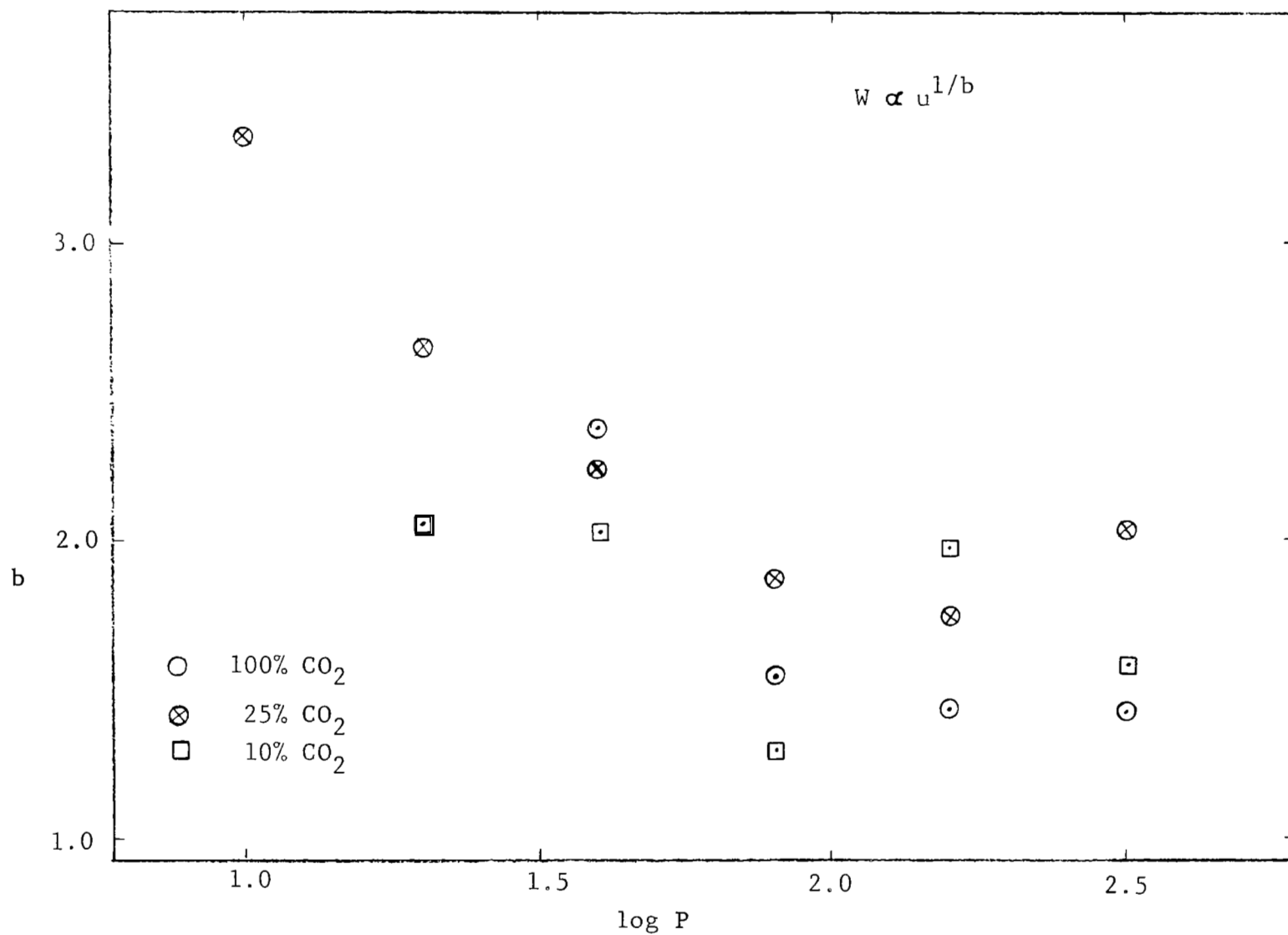


Fig. 6 Exponent for Equivalent Width Dependence on Optical Density as a Function of Pressure

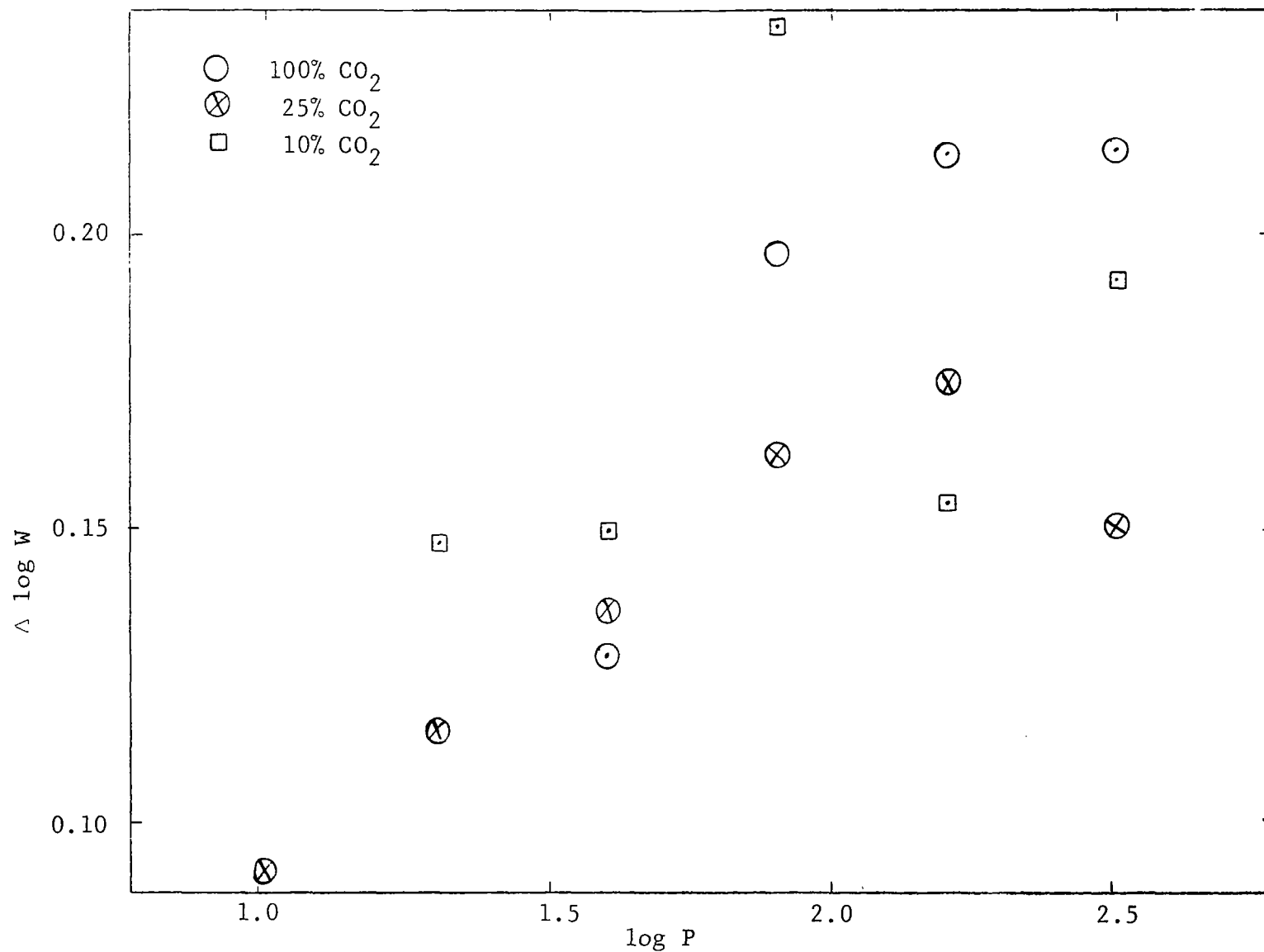


Fig. 7 Correction to Equivalent Width for Doubling the Amount of Absorbing Gas

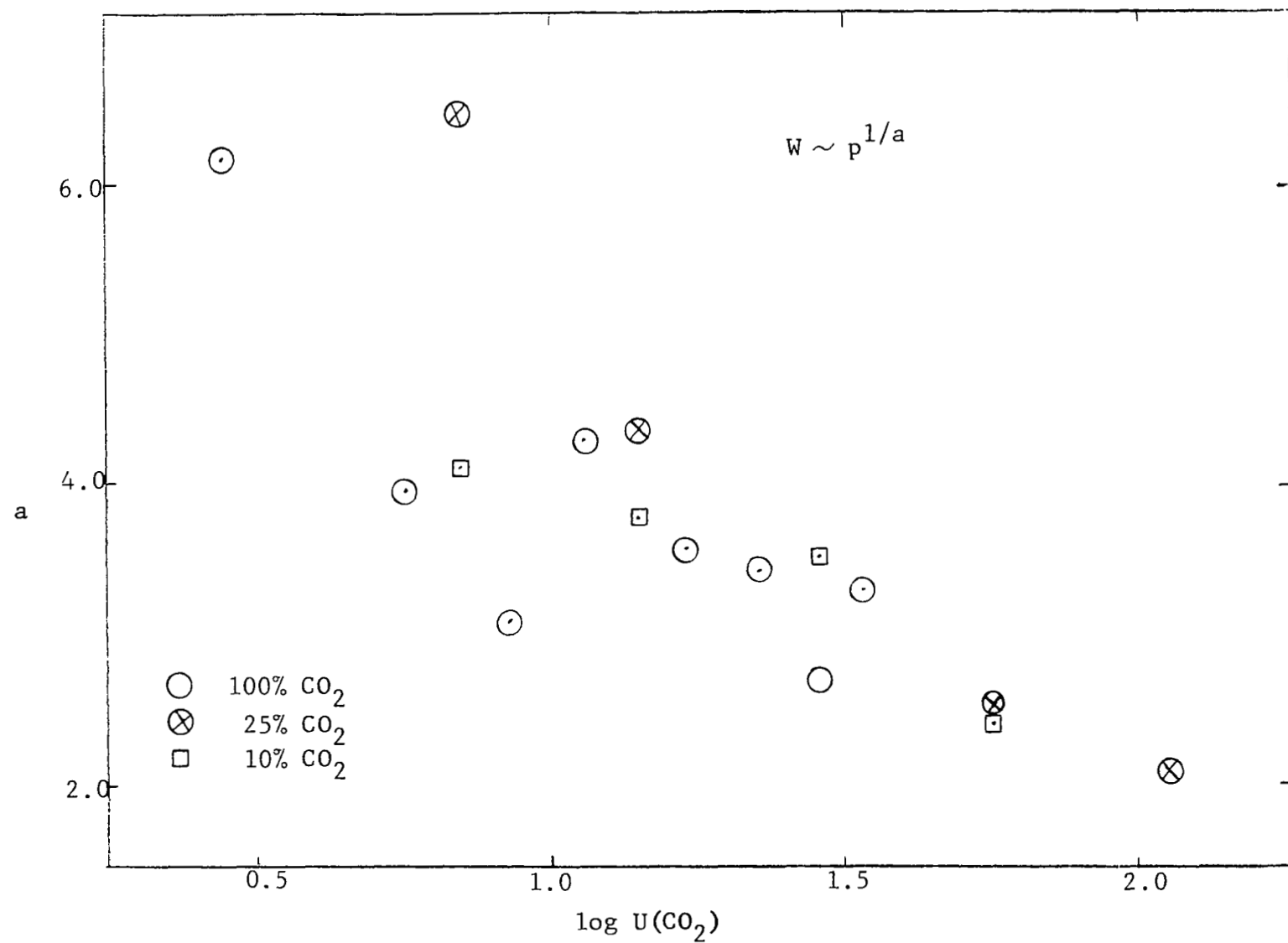


Fig. 8 Exponent for Equivalent Width Dependence on Pressure as a Function of Optical Density

and $\Delta \log W = 0.15$.

The results obtained in this analysis are consistent with the general behavior of absorption with pressure and optical density (see Appendix 3.4). For curves of constant pressure, at a given value of the product pu , the exponent of u is lower for lower pressures because the transition to the square root region ($b = 2$) and the transition beyond this region ($b > 2$) occur at lower values of the product pu for lower pressures. Thus it is expected, and observed by (OK), that the values of $(1/b)$ should decrease gradually as the pressure is increased. Similarly, the exponent $(1/a)$ of the pressure is a decreasing function of optical density, and only approaches a square root dependence at the largest optical densities considered. These results imply that the extrapolation of the laboratory data to Martian CO_2 abundances should be carried out with a pressure dependent value for $\Delta \log W$; if at the low pressures one uses the square root approximation, the pressure will be underestimated. The surface pressures obtained with the pressure dependent extrapolation and the square root approximation are compared with the values given by (OK) in Table III. (The details of these extrapolations are given in Appendix 3.5).

Table III

PRESSURE DEPENDENT AND SQUARE ROOT
PRESSURE DETERMINATIONS

Gas Mixture <u>% CO₂</u>	Surface Pressure (mb)		
	<u>Pressure Dependent</u>	<u>Square Root</u>	<u>(OK)</u>
100	13.4	9.6	9.6
25	14.0	12.0	16.0
10	24.0	15.0	19.0

An alternate method of presenting the data offered by (OK) provided upper and lower limits of the Martian pressure from a log-log- plot of equivalent widths vs. the product pressure times optical density. Their analysis of this plot for the 100 percent CO₂ data suggested that for pressures in the range from 20 mb to 40 mb, the equivalent widths can be expressed by

$$\log W = \frac{1}{2.32} \log p_u - 0.65 .$$

This is in fair agreement with the results given above, where the average value of b for these pressures is 2.4, and it implies a correction to $\log W$ for doubling the amount of gas of $\Delta \log W = 0.13$. They suggested that for curves of constant pressure, those with pressures < 20 mb approach this 20-40 mb curve asymptotically from the left, while those for pressures > 40 mb approach this curve from the right. Since all the pressures obtained with the first method were less than 20 mb, the intersection of the 20-40 mb curve with the horizontal line

representing the Martian equivalent width should provide an upper limit for the pressure. The lower limit is obtained by estimating the location of the intercept at low pressures, for which there are no measured equivalent widths. The upper limit is determined with much greater precision than the lower limit. The method of obtaining upper and lower limits for the pressure appears to be physically reasonable (see Appendix 3.3), and the values of these limits are probably more significant than the value of $P = 17$ mb.

In (OK), the upper limit was established using the Martian CO_2 abundance of 46 m-atm and an equivalent width of 15.8 \AA for the 1.6μ bands on Mars; no error or uncertainty was attached to either the abundance or equivalent width. We have considered the effect on the pressure limits of the uncertainty in the abundance and, based on Kuiper's comment⁵¹ that the accuracy of the absorption measurements is between ± 10 and ± 15 percent, have considered the effect of ± 10 percent variations in the equivalent widths. These results are summarized in Table IV.

Table IV

UNCERTAINTY IN PRESSURE FOR ERRORS IN CO₂
ABUNDANCE ϵ_1 (Δu) AND EQUIVALENT WIDTHS ϵ_2 (ΔW)

% CO ₂	Upper Limit (mb)	ϵ_1 (Δu)	ϵ_2 (ΔW)	$\sum \epsilon_{12}$	Range of Upper Limit (mb)
100	11.7	+5.8, -2.9	± 2.9	+8.7, -5.8	20.4 -5.9
25	17.6	+8.8, -4.4	± 3.5	+12.3, -7.9	29.9 -9.7
10	22.2	+11.1, -5.5	± 3.3	+14.4, -8.8	36.6 -13.4

The effect on the adopted value of 17 mb of uncertainties in the Martian CO₂ abundance and the 1.6 μ CO₂ equivalent width was estimated from the intersections of lines representing maximum and minimum values of equivalent width and abundance on a log-log plot of equivalent width vs. pressure; the adopted value of pressure becomes 17 mb (+14, -9). (The error for the abundance used here does not account for the temperature uncertainty, i.e., it is assumed the temperature is 200°K.)

3.2.4 The Pressure Derivation of Moroz

Moroz¹⁶ measured the equivalent widths of the strong CO₂ bands near 1.6 μ (four bands) and at 2.06 μ in the spectrum of Mars. Using a curve of growth obtained from observations of the same bands in the telluric spectrum, he could subtract the telluric component and obtain the Martian equivalent widths. Again using the observations of the telluric bands, he fitted them with an Elsasser band model^{52,53} to derive a value for the band

intensity S . Knowing S , he could apply the Elsasser model to the Martian bands and solve for the product of the optical density u and the surface pressure p . Moroz was compelled to rely on the same observation of the weak $5\frac{1}{2}$ band as the other workers to obtain a value of u . He adopted the KMS value of $u = 55 \pm 20$ m-atm and found a surface pressure of 15^{+15}_{-5} mb.

We have repeated Moroz' calculations correcting an apparent arithmetical error and using slightly different values for some of the parameters. The most important of these revisions were a change of the adopted telluric CO_2 abundance (from 320 cm-atm⁵⁸ to 260 cm-atm)^{59,61} and the inclusion of the temperature dependence of the half width of the rotational lines and of the band half width. We also used the same value of u which was adopted in our discussion of the CO_2 abundance. The net effect of these changes was small since they tended to compensate each other. The assessment of uncertainties was less direct than for the other two pressure determinations since we did not exactly duplicate Moroz' analytical technique. Uncertainties were added to his maximum deviations to account for errors in the measurement of the equivalent width and the band half width. The final result was

$$P = 13^{+25}_{-8} \text{ mb.}$$

The details of the calculation of uncertainties may be found in Appendix 3.6.

3.3 Conclusions

The most important conclusion that can be drawn from the infrared observations is that the Martian surface pressure is lower than the previously accepted value of 90 mb provided by Dollfus' polarization measurements. The largest contribution to the uncertainty in these pressure determinations is the error associated with the CO₂ abundance. Although the ultimate accuracy of the pressure measurement with these infrared techniques is limited primarily by the precision with which the abundance is known, when the pressure is calculated using the extreme limits of all parameters, the upper limit is about two-thirds of the previously accepted 90 mb.

It should be emphasized that all three pressure determinations (KMS, OK and Moroz) utilize the Martian CO₂ abundance determined from the single spectrograph plate obtained by (KMS). The extreme limits of the CO₂ abundance are included in the uncertainty given for the pressure, but since only one measurement exists there is at least a remote chance that subsequent measurements will fall outside the error limits assigned to the abundance measurement, and every effort should be made to obtain corroboration of these observations.

The large uncertainty attached to the KMS pressure determinations should not be taken to imply their calculations are less accurate than either OK or Moroz. There are two reasons why these uncertainties are higher than for OK or

Moroz. First, since we are considering relative errors, a higher pressure is given a larger uncertainty than a lower one, even if the relative errors are equal. Second, the method used by KMS to calculate the pressure is very straightforward. For the empirical method used by OK, the determination of the uncertainty cannot be accomplished with the statistical approach, and one is led to an empirical estimate of the uncertainty. In the case of Moroz, there was insufficient time to completely evaluate the uncertainty associated with his pressure determination, so this error should also be considered rather approximate. In comparing the uncertainties associated with the three pressure determinations (KMS, OK and Moroz), a simple tabulation of errors or a graphical display of errors bars is a convenient portrayal of the results, but it is necessarily unfair to KMS.

The surface pressures obtained with the three methods vary by a factor of two even when the same CO_2 abundance is used. This is an indication of the uncertainty involved in using the strong band absorption data. Two possible sources of this uncertainty are (1) the error associated with the strong band absorption measurements, and (2) the expression of this strong band absorption in terms of an absorption coefficient or equivalent width.

In KMS the strong band absorption data was represented in three different ways: (1) an absorption coefficient for non-overlapping pressure dependent lines, (2) a comparison of

Martian and laboratory absorption spectra, and (3) an assumption that a representation of the equivalent widths with the strong line approximation is valid. The first two appear to be justified, and although the validity of the assumption that the equivalent widths fit the strong line approximation is not completely obvious, all three methods yield approximately the same pressure. Since this pressure is approximately twice that given by Moroz, a consideration of the assumptions made in the latter work is in order.

Moroz assumes that the absorption can be represented by the Elsasser band model, and uses the complete expression for this model rather than the strong line approximation. While the Elsasser band may be a good representation of CO₂ absorption at room temperatures, higher pressures, and shorter path lengths, there is no experimental data available that would indicate the applicability of this band model for CO₂ at the atmospheric conditions on Mars. Thus Moroz seems to have traded one assumption, - the use of the Elsasser band model, - for another, the use of the strong line approximation. This appears to be one real difference between the procedure of KMS and Moroz, since Moroz' equivalent widths are essentially the same as those used by KMS. Additional experimental and analytical evaluation of equivalent width data is required if this point is to be further clarified.

The empirical method employed by OK could, in principle, eliminate the uncertainties inherent in the choice of a given band model or approximation to describe the Martian CO₂ absorption. However, it is not possible to simulate the Martian atmosphere completely with existing laboratory equipment and measurements of the equivalent width do not exist for the range of pressures and CO₂ optical densities that occur on Mars. Thus some extrapolation is required to determine the Martian pressure, and some choice of band model, (i.e., dependence of equivalent width on both pressure and optical density) is implicit in this extrapolation. As indicated above, it is possible to determine, at least approximately, the nature of this extrapolation from the available equivalent widths, but this method is limited by the lack of data at low pressures and long path lengths. While some form of pressure dependent extrapolation was used in determining the surface pressure of 17 mb, the degree of intuitive judgment required is such that an independent observer is unlikely to obtain this same value. The upper limit for the pressure given by OK is reasonably well defined, and is probably more significant than the value derived for the pressure. The most valuable contribution that can be offered with this empirical method would be to increase the available path length. Since the present path is the order of ten percent of that required to simulate Martian conditions, it is unlikely that a direct comparison can be made, but any

extension of available path lengths would provide a stronger basis for an empirical extrapolation.

4. SUMMARY AND GENERAL CONCLUSIONS*

In Section 2 of this report we have reviewed the polarimetric work of Dollfus and indicated that even within the framework of his basic assumptions considerable uncertainty must be attached to the value of the surface pressure he derives. Our evaluation of the four different methods used by Dollfus suggests that method one is the most accurate of the four. Both of these conclusions agree with Dollfus' own assessment of the accuracy of this part of his work. Treating the angular dependence of the surface brightness of the disk of Mars in a different manner than that of Dollfus, we have avoided an unnecessary separation of variables and derive a lower value for the ratio of atmospheric to surface brightness (B_a/B_s). This in turn leads to a lower value of the surface pressure (63 mb). We have indicated that this value contains uncertainties due to the photometric measures used to determine B_s as well as those due to the polarimetric observations. The low error of the latter is a tribute to Dollfus' skill as an observer, but the real problem arises in attempting to interpret the measurements once they are made. A close look at the assumptions of pure Rayleigh scattering in an atmosphere whose composition is identical with that

* Underlined phrases indicate topics which require additional research effort.

of the Earth indicates that, while these may be acceptable as a first approximation, they cannot be relied on for an accurate determination. The spectroscopic identification of considerable quantities of CO₂ in the Martian atmosphere - aside from the direct implications it has for the surface pressure - indicates that the composition of that atmosphere is not the same as ours. Use of various mixtures of gases leads to a range of surface pressures. The presence of the blue haze and observations of clouds and dust storms are strong indications that some quantity and size distribution of scattering particles must be present in the Martian atmosphere at all times. In addition, the phenomena associated with the blue haze have been interpreted by some astronomers as being due to absorption, or some combination of absorption and scattering. The effect of including a consideration of these processes has been shown to be complete uncertainty regarding the surface pressure corresponding to the polarimetric observations. It seems very probable that polarimetric studies can be used to obtain information about the particulate matter suspended in the atmosphere once the atmospheric thickness has been determined by other means.

The attempt by Musman to establish an upper limit to the surface pressure by interpreting the ultraviolet albedo as being due entirely to a Rayleigh scattering atmosphere is subject to these same restrictions. If there is no absorption, this upper limit should be valid - the presence of scattering particles would imply a lower value for the surface pressure.

However, the presence of absorption would again render the problem indeterminate, as Musman notes in his paper. Perhaps the most interesting point about Musman's work is that he has made the same assumptions as Dollfus and yet derives an upper limit of 30 mb to the surface pressure. This implies either (1) the Martian atmosphere absorbs strongly in the region of 3300 Å where the photometry used by Musman was done, or (2) some distribution of particles must be present which would cause the results obtained by Dollfus to be overestimates. We have looked into this question in some detail and have shown that agreement between the visible and ultraviolet determinations can be made with an appropriate particle distribution which leads to a true gas pressure of approximately 17 mb. This treatment ignores the possibility of absorption and is a definite simplification in that only limited particle sizes are considered rather than a mixture. It is intended primarily as an indication of the kind of indeterminacy which exists in this problem.

The spectroscopic analyses are not subject to these uncertainties and thus have a distinct advantage in this respect. The principal weakness in the pressure determinations based on the spectroscopic data appears to be the fact that all these determinations rely on the same single Martian spectrogram for their value of the CO₂ abundance. The uncertainty associated with interpretations of this spectrogram can be best appreciated

by inspection of the published densitometer tracing of the region of interest. The comparison of this tracing with a laboratory spectrogram and a tracing of the solar spectrum in the same region given by Owen is reproduced here to illustrate this point (Figure 9). The need for additional observations is readily apparent. In addition, the work of Hanst and Swan suggests that the laboratory calibration of the $5\mu_3$ line intensities is not a closed question. More work must be done on this problem before a reliable abundance determination can be made. At the present time, available evidence (including preliminary work by Inn⁷⁶) appears to favor the higher value of the CO₂ abundance adopted in this report: 45 ± 25 m atm. This situation may change as additional data become available. (See note p. 76.)

The strong line data are better established than the abundance since three independent sources are available. In addition, Kaplan et al. used data obtained by Kuiper which were not used by Owen and Kuiper, making this a fourth set of observations (Sinton, Kuiper 1 and 2 and Moroz). We have compared the equivalent widths of the 1.6μ bands measured by Kuiper and by Moroz and find that they agree to within $\pm 15\%$. The 2.06μ band equivalent width used by KMS is in similar agreement with the value measured by Moroz. Since we have used the same value of the CO₂ abundance in evaluating all three pressure measurements, any large differences in the derived surface pressures must be due to the different methods of interpreting the strong line data.

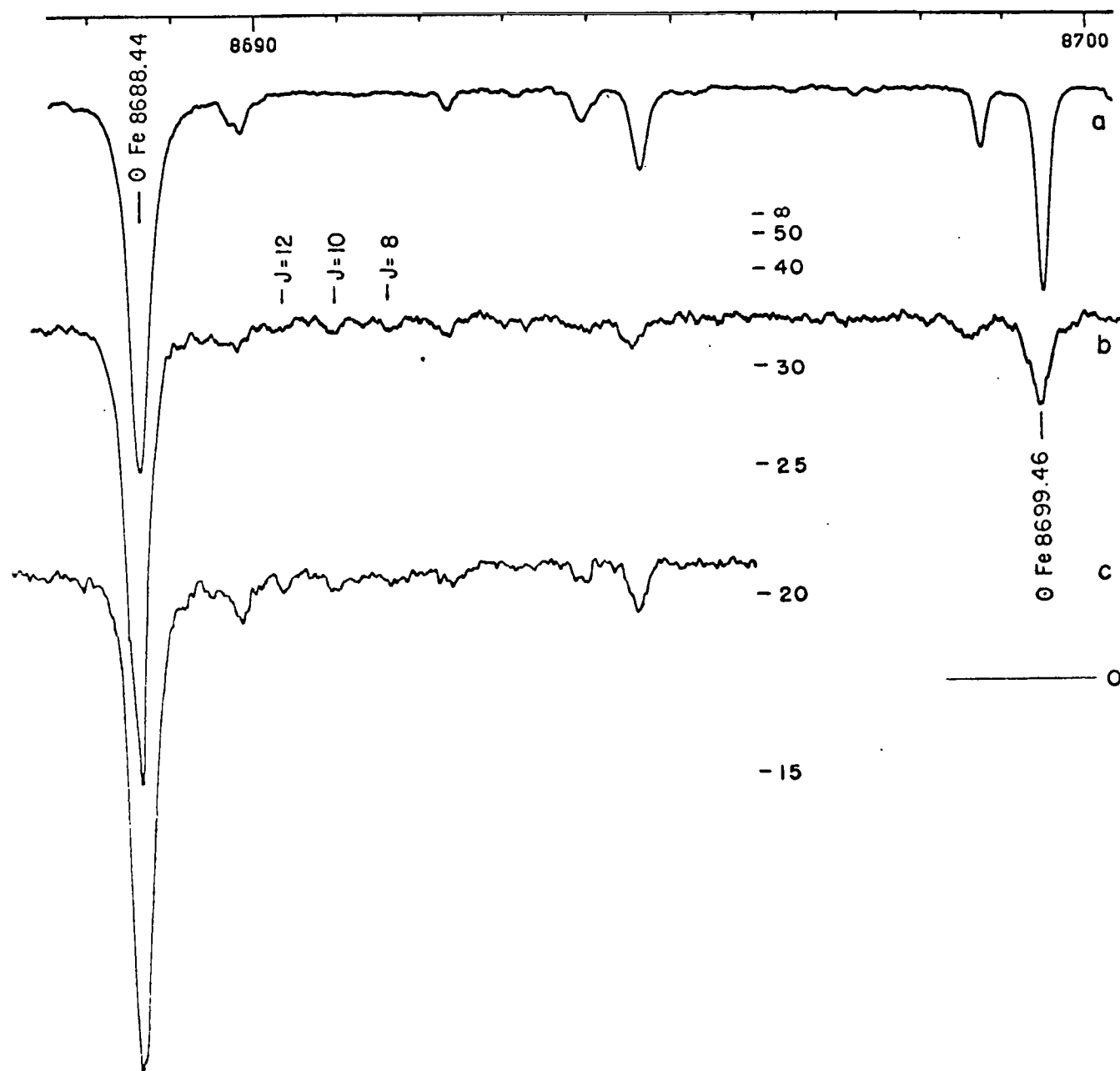


Fig. 9: a) Solar Spectrum from the Liège Photometric Atlas, (b) Mt. Wilson Mars spectrogram, (c) Laboratory comparison (sun + CO₂). Note presence of three rotational CO₂ lines in (b) and (c).

On the basis of the available evidence, it doesn't appear to be possible to discriminate among the various methods of analysis which have been used. In each case, certain assumptions have been made and there is simply not enough laboratory data obtained under the right conditions (very low pressures and long path lengths) to test the validity of the assumptions. The same strong line assumption used by KMS and OK leads to results differing by nearly a factor 2 when applied to the 2.06μ bands and the 1.6μ bands. We have suggested that the equivalent width is probably better represented by the relation $W \propto u^{x_1} p^{x_2}$ than by the strong line version $W \propto (up)^W$. This point has also been made by Howard, Burch and Williams⁴⁷ on the basis of their laboratory studies. These authors specifically comment on the failure of the Elsasser model to accurately predict absorption because of its use of the assumption that the dependence of the equivalent width on u and p is the same. This comment has obvious relevance to the work of Moroz since he used this model to reduce his observations.

The results of this review are summarized in Table V. The upper limit deduced by Musman has not been revised since the possible presence of absorption renders it too uncertain. The same argument also applies to Dollfus' results; the value of 63 mb represents our evaluation of the ratio B_a/B_s . We have not associated a relative error with this number since the possible presence of absorption or scattering particles represents an even greater uncertainty than errors in the polarimetric

or photometric observations.

Absolute lower limits can be introduced corresponding to the surface pressure exerted by an atmosphere consisting entirely of CO_2 . These have a range of 2 to 6 mb; the amounts of gas represent the extreme upper and lower limits which have been assigned to the abundance in this report.

It should be evident from Table V and the previous discussion that it is not yet possible to deduce a number for the Martian surface pressure in which much confidence can be placed. This point is emphasized by the value of the surface pressure deduced by Hanst and Swan using their revised value of the CO_2 abundance and the KMS treatment of Sinton's 2.06μ data. However, there is very good hope that with additional data on weak CO_2 bands in the Martian spectrum, additional laboratory calibrations of these bands, and studies of the fit of band models at low pressures and high optical densities, the large uncertainties presently associated with these determinations will be reduced. Despite the remaining uncertainties, the present range of values for the Martian surface pressure appears to have much greater reliability than the numbers which have been quoted in the past. It would therefore appear that the design of spacecraft for probing the Martian environment should not proceed on the assumption that the surface pressure is 90 mb, but rather should allow for the more severe problems that will be experienced if a lower value for the pressure is correct.

Table V

RECENT DETERMINATIONS OF MARTIAN SURFACE PRESSURE

Author and Technique	Original Estimate (mb)	Revised Estimate (mb)	Remarks
1. Dollfus Visual polarimetry	90	63	Assumes pure Rayleigh scattering atmosphere composed of air.
2. This paper Dollfus' polarimetry	51	--	Assumes pure Rayleigh scattering atmosphere composed of $1/3 \text{ CO}_2 + 2/3 \text{ N}_2$.
3. Musman UV photometry	27 (upper limit)	--	Assumes pure Rayleigh scattering atmosphere composed of air, no absorption, zero surface albedo.
4. This paper Musman's argument	22 (upper limit)	--	Assumes pure Rayleigh scattering atmosphere composed of $1/3 \text{ CO}_2 + 2/3 \text{ N}_2$, no absorption, zero surface albedo.
5. This paper Dollfus' polarimetry and Musman's argument	17	--	Compatible surface pressure: assumes atmosphere composed of $1/3 \text{ CO}_2 + 2/3 \text{ N}_2$ plus 8×10^8 ice particles of 0.2μ diameter per cm^2 -column.
6. KMS Spectroscopy	25 ± 15	33 ± 30	Revision based on Martian CO_2 abundance of 45 ± 25 m-atm.
7. OK Spectroscopy	17 ± 3 (p.e.)	37 (upper limit)	" " " " " " "

Table V (Cont'd)

Author and Technique	Original Estimate (mb)	Revised Estimate (mb)	Remarks
8. Moroz Spectroscopy	15 $\begin{smallmatrix} +10 \\ -5 \end{smallmatrix}$	13 $\begin{smallmatrix} +25 \\ -8 \end{smallmatrix}$	Revision based on Martian CO ₂ abundance of 45 ± 25 m-atm.
9. Hanst and Swan Spectroscopy	56 \pm 31	--	Based on Martian CO ₂ abundance of 28 ± 13 m-atm.

Since we have stressed the tentative nature of these values for the surface pressure, it seems pertinent to close with some remarks about the effect of new results on presently available estimates. This discussion is limited to the spectroscopic method. The largest change is likely to occur in the value of the CO₂ abundance. As we have mentioned above, an indication of the present uncertainty in this quantity is provided by the work of Hanst and Swan, which also offers a clue as to the effect a revision of this value will have on the surface pressure. An increase in the intensity S of the rotational lines of the 5 $\frac{1}{2}$ /₃ band will lead to a lower CO₂ abundance and consequently a higher surface pressure. Conversely, if a remeasurement of the equivalent widths of these lines in the Martian spectrum suggests that the values determined by KMS are too small, the CO₂ abundance must be increased and the surface pressure decreased. Finally, if the atmospheric temperature which we have chosen in our analysis proves to be too low, the CO₂ abundance will be increased and the pressure decreased. Obviously a reversal of any of these changes will lead to consequences which are also reversed.

Note added in proof: Dr. Inn has informed us that he has completed his remeasurement of the intensity of the R branch of the 5 $\frac{1}{2}$ /₃ CO₂ band. For $J \geq 8$, he derived an absorption coefficient of 0.33 cm⁻¹/km amagat, in excellent agreement with Rank's value of 0.32 cm⁻¹/km amagat.

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APPENDICES FOR SECTION 2

FOREWORD

This collection of appendices forms Part II of our review of recent studies of the Martian atmosphere. Part I contains summaries of the material being reviewed with our comments and evaluations. It was our intention that Part I should be a self-contained report including enough detail to satisfy the general reader.

The appendices presented in this section (Part II) contain supporting calculations for the conclusions reached in Part I as well as additional discussion of certain topics which were only briefly treated in the main text. No attempt was made to prepare Part II as a self-contained document since all of the material it contains refers to the various sections of Part I.

References to these appendices are made at appropriate points in the text of Part I. The reference numbers consist of two digits, the first of which designates the section of Part I to which the appendix refers (2 or 3) while the second digit is a running number for the appendices referring to that section.

PART II - APPENDICES

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2.1 Discussion of the Assumptions in the Polarimetric Equation

The Ratios (B_V/B_0) , (B_θ/B_0) , $a(\lambda)$

It is not clear from Dollfus' publications whether or not the first two ratios are evaluated at the respective θ and V . However, in discussion²¹, Dollfus said that he took these ratios directly from the photometric curves which he published²², with appropriate interpolation. These curves are reproduced here in Figure A-1. In this figure 1.0 on the vertical axis corresponds to the ratio at the center of the disk for zero phase; hence, points on these curves give the brightness for various V and θ in terms of the brightness for $V = \theta = 0$. Thus the points on the curve give the quantity

$$\left[\frac{B_V}{B_0} \cdot \frac{B_\theta}{B_0} \right]$$

directly. It is clear from Figure A-1 that the ratios (B_V/B_0) and (B_θ/B_0) depend on θ and V respectively. For example, at $V = 0^\circ$ (B_θ/B_0) is symmetrical about $\theta = 0$, but at other values of V it is not. From this figure it would be possible to deduce curves for these ratios for various θ and V respectively, and so to allow for these variations. Dollfus, however, indicated²¹ that B_0 is for $V = 0$ and $\theta = 0$, hence the ratio B_V/B_0 was for $\theta = 0$ and the ratio B_θ/B_0 for $V = 0$.

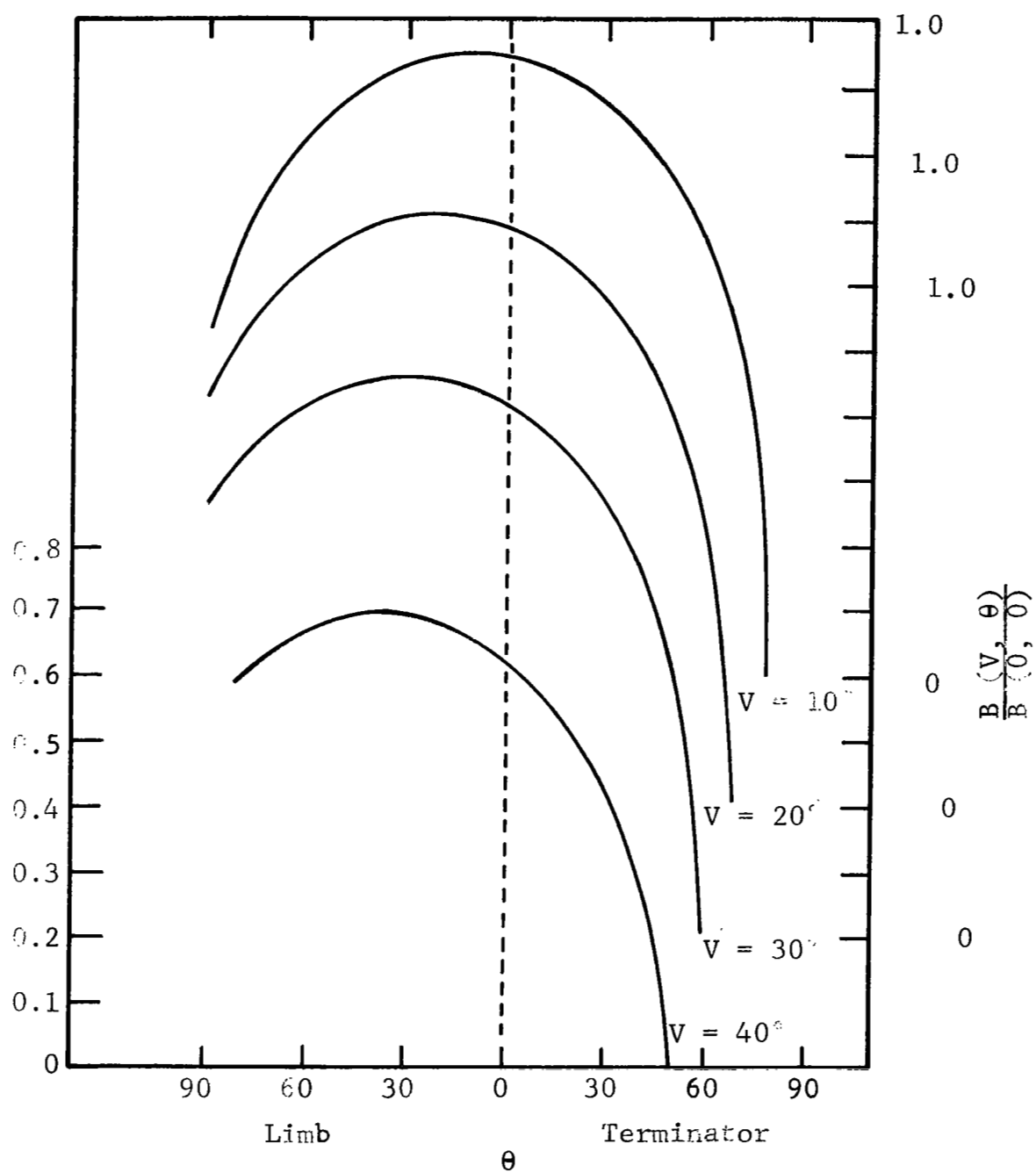


Fig. A-1 Mars Photometric Data (Dollfus)

In Appendix 2.2, where his data reduction is discussed, it is shown that this approximation has had the result of raising the value of B_a/B_s , and consequently the pressure. If no attempt is made to separate these two dependences, the correct ratio $B(V, \theta)/B(0,0)$ can be read directly from interpolations on Figure A-1. It is not clear why Dollfus did not do this himself.

The wavelength dependence for B_s , manifested in $a(\lambda)$, is also given in the same paper²² but only for $V = 29.2^\circ$. Thus, the V -dependence of this quantity is undetermined. Some recent data for limonite made available by Coulson²⁴ does show a V -dependence; from $V = 5$ to 50° there was a 9% variation between the two wavelengths 0.643 and 0.492μ . However, the polarimetric curve for this limonite sample does not fit the one for Mars, so that there is no justification for using this data. Only a slight θ -dependence is shown²² over the wavelength range 0.54μ to 0.63μ . Since Dollfus' most accurate work was conducted at one wavelength ($\lambda_0 = 0.61\mu$), small uncertainties in $a(\lambda)$ are not very important.

The Quantity $\Delta(\theta, \lambda)$

Dollfus omitted the λ -dependence of this quantity and stated²¹ that he thought it was negligible. He obtained $\Delta(\theta)$ by making measurements on Mars⁶ keeping $V \leq 15^\circ$. Since the atmospheric polarization varies as V^2 for small V , it is not significant in this range, so that the surface effect is measured.

Dollfus stated that atmospheric effects were taken into account²⁰ in the $\Delta(\theta)$ plot, but in the text he does not say how. Later²¹ he explained this statement: the polarimetric results that he used were obtained after very careful selection, based on all the photographic, photometric and polarimetric data available. In this way he was able to select the observations made when the Martian atmosphere was clearest. In an endeavor to allow for residual effects, he always selected the values (for a clear atmosphere) giving the lowest values for P. In this way he was able to construct a plot of $\Delta(\theta)$ as a function of θ . He also allowed for the small atmospheric Rayleigh component in the polarization. His results are shown in Figure A-2 along with some curves fitted during the present study; those for emery and limonite were obtained from data taken by Dollfus²³. Dollfus did not include a curve in his figure, but in the text^{5,6,20} mentioned a value of $\Delta(\theta) = -0.004$ at $\theta = 60^\circ$, and this was what he used in the data reduction²¹. Dollfus later stated²¹ that he thought this value of $\Delta(\theta)$ should be raised to around -0.003 or -0.002 , judging from laboratory measurements on limonite (in his papers^{5,6,20} Dollfus shows that the polarimetric curve for limonite fits the Mars curve better than those for any other of a large number of terrestrial materials tested), and said that -0.003 should be used in preference to -0.004 .

More detailed calculations with emery showed that $\Delta(\theta)$ varied significantly with V . However, Dollfus pointed out²¹ that emery was a transparent crystal, while limonite was

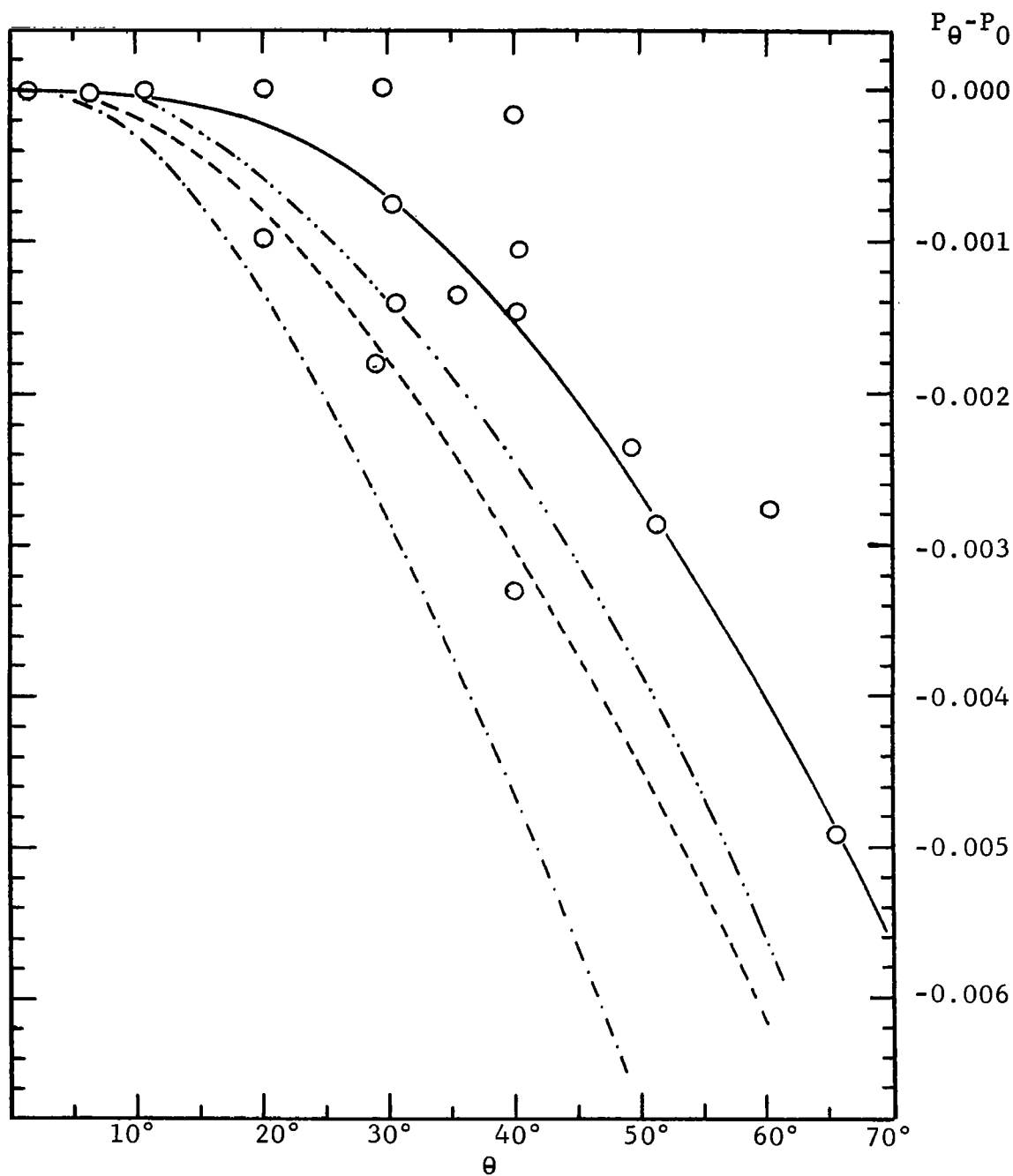


Fig. A-2 Values of $\Delta(\theta)$ given by Dollfus in Figure 36 of [6]

- Powdered Emery - $V = 0^\circ$
- Powdered Emery - $V = 20^\circ$
- Powdered Limonite - $V = 0^\circ$
- Curve drawn through
 $\Delta(\theta) = -0.004$ at $\theta = 60^\circ$.

not, and that the analogy should not be taken too seriously. During the visit to Paris²¹, Dollfus made some measurements on limonite and showed that $\Delta(\theta)$ varied by about 0.001 between $V = 0^\circ$ and $V = 40^\circ$. Since this was the same order of magnitude as the scatter in the laboratory results, the variation is small and not significant. Application of the result to Mars does depend on the validity of the identification of the nature of its surface (bright areas in this case) which cannot yet be regarded as completely established.

Wavelength Dependence of $P_s(V, \lambda)$

At the time Dollfus published his work, there was no data on the wavelength dependence of $P_s(V, \lambda)$. Since then, he has measured the wavelength dependence of limonite and has kindly furnished this information for use in the present study²¹. It will be seen in Appendix 2.2 that it is the difference $P_s(V, \lambda_0) - P_s(V, \lambda_1)$ that is required, where $\lambda_0 = 0.61\mu$ and $\lambda_1 = 0.53\mu$. The following table shows this difference deduced from Dollfus' figures.

(Polarization in units of 0.001)

V°	P _{0.63} -P _{0.55}	V°	P _{0.63} -P _{0.55}
		22.5	-0.4
3	-0.73	25	-0.3
5	+0.3	27.5	--
7.5	+1.2	30	0.00
10	+0.2	35	-1.4
12.5	-0.6	40	+0.9
15	+1.2	45	-1.1
17.5	+0.5	47.5	-2.7
20	+0.5	50	-6.8

It is fairly clear that up to $V = 40^\circ$ the effect is not very significant. (Note: the wavelengths given in the table correspond to laboratory studies and are not identical to the wavelengths at which the Mars observations were made. The band pass of Dollfus' filter-detector combination is sufficiently wide that this difference is felt to be insignificant.)

2.2 Discussion of the Deduction of B_a/B_s from Polarimetric Measurements

Dollfus used the polarization equation (5) in four different ways to deduce the brightness ratio B_a/B_s . Only in the first method was the work done at a single wavelength. The following analysis shows the first method to be quite the most reliable; a conclusion with which Dollfus fully agreed²¹. He pointed out that he regarded the other three methods primarily as checks on method 1. If they had not given similar results, a major error in formulation would have been indicated.

First Method

The polarization was measured at the center and at the edge of the disk at a wavelength of 0.61μ . The difference was taken, giving

$$P(V, \theta) - P(V, 0) = \Delta(\theta) + \frac{B_a}{B_s} \cdot \frac{B_o}{B_V} \frac{\sin^2 V}{2} \cdot \left[\frac{B_o}{B_\theta} \sec \theta - 1 \right]. \quad (6)$$

This method of writing the equation^{5,6,20} provides additional confirmation for the suggestion that the ratios (B_V/B_o) and (B_θ/B_o) were used incorrectly. Equation (7), given below, shows the modification that arises when the V- and θ -dependences of P_s are not separated. Dollfus gives his data in a straight line plot^{5,6,20} of equation (6) which is shown in Figure A-3. A line was fitted to the plotted points by least squares giving a slope of 0.0363 ± 0.0055 , in agreement with Dollfus' figure of 0.036.

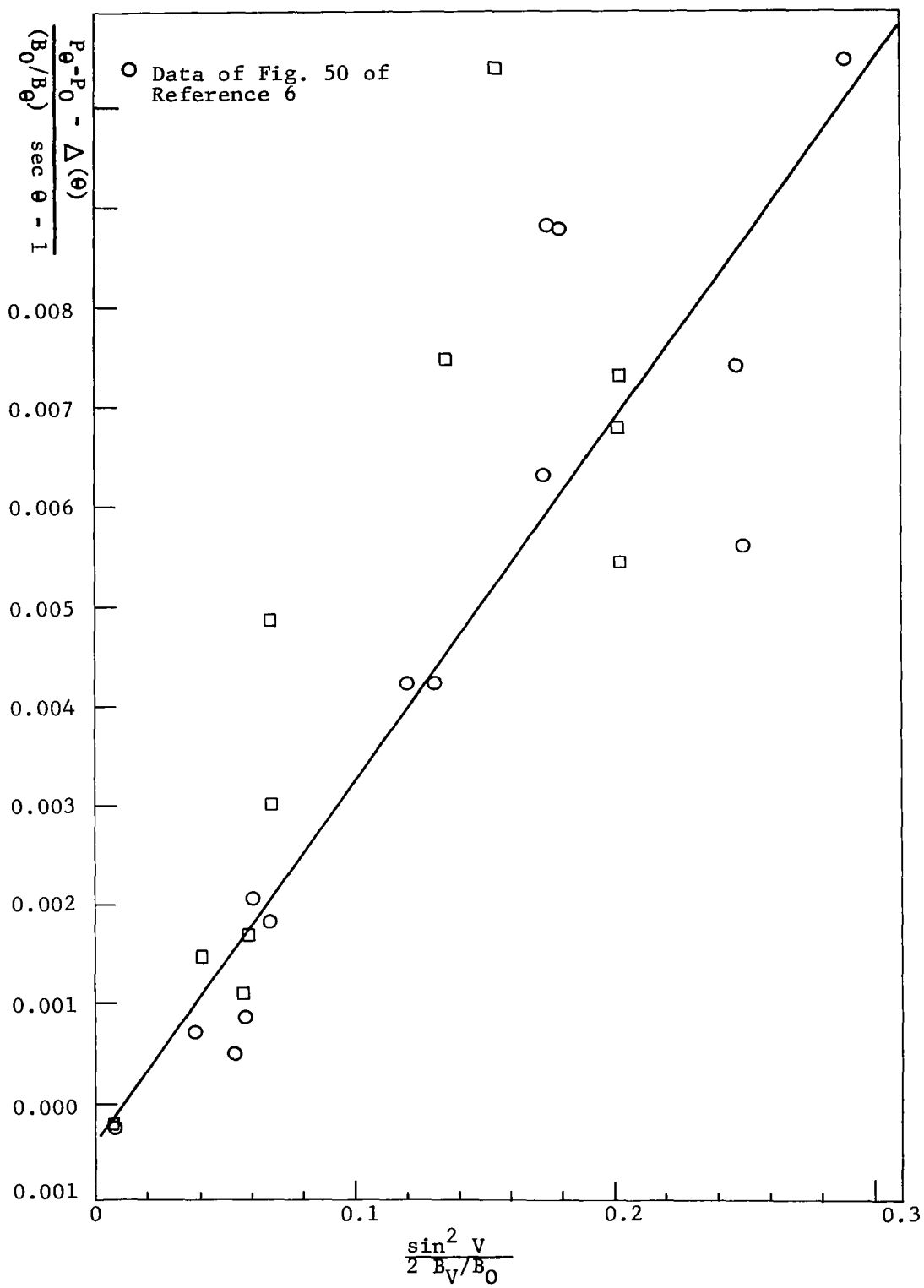


Fig. A-3 Atmospheric Polarization. Line fitted by least squares.

Dollfus supplied the original polarization measurements which were used in this method to allow a check to be made²¹. He also supplied copies of his photometric curves (Figure A-1). This polarimetric data was collected from February 1948 until July 1952. Measurements were made between $V = 6.2^\circ$ and 43.8° ; for $\theta = 65^\circ$ towards the limb, and at $\theta = 30^\circ, 40^\circ, 55^\circ, 60^\circ$ and 65° towards the terminator.

In order to check on the use of the photometric data, the polarimetric data was reduced taking (B_V/B_O) at $\theta = 0$ and (B_θ/B_O) at $V = 0$. These points are shown in Figure A-3 with the exception of the three highest values which are off this scale. There is an appreciable discrepancy between Dollfus results and the new ones. The primary reason for this probably lies in the interpolation made on the photometric curves in Figure A-1. The results are very sensitive to the shapes of these curves, especially at high angles towards the terminator. The brightness ratios at the sub-solar points were also published²², but from these, the curve for $V = 40^\circ$ had to be estimated (Figure A-2). These four curves were then used to derive curves as a function of V for the θ values required. It appeared that Dollfus used a similar method²¹, but during our visit he did not have the details of his data reduction available. One other source of error is the angle θ . Dollfus estimated this to the nearest 5° , and he could have selected some points slightly differently than we did for his own calculations.

The new value of (B_a/B_s) is approximately 0.048 for this data, but Dollfus' original figure of 0.036 must be considered the more reliable because of possible additional factors in the data analysis which he may have forgotten over ten years. The comparison does show two things, however. Firstly, the error of $\pm 15\%$, deduced from a least squares fit to his points, is not very meaningful as an uncertainty because of the other factors just mentioned. Secondly, Dollfus does appear to have used this method to reduce his data.

It is pertinent to analyze the data differently, using the equation

$$P(V, \theta) - P(V, 0) = \Delta(\theta) + \frac{B_a}{B_s} \frac{\sin^2 V}{2} \frac{B(0,0)}{B(V, \theta)} \sec \theta - \frac{B(0,0)}{B(V,0)} \quad (7)$$

The two ratios $B(0,0)/B(V, \theta)$ and $B(0,0)/B(V,0)$ are also obtained from the interpolations on Figure A-1, but do not now make the approximation of separating the variables. The results are shown in Figure A-4. The line is at least squares fit to 13 of the points and has a slope of 0.0147 ± 0.0072 with an intercept of $\Delta(\theta) = -0.009$. Such an interpretation assumes $\Delta(\theta)$ to be constant over the range of the experiment. There were three points for which $\theta > 55^\circ$; these are marked as squares in the figure. Omitting these in the calculation gives a slope of 0.015 ± 0.0046 and an intercept of $+0.0014$. Hence this low value to the slope cannot be put to the values assumed for $\Delta(\theta)$. Another calculation was made with different interpolation curves for the photometric data and yielded $B_a/B_s = 0.0175$ with an intercept of $\Delta(\theta) = 0.001$, but this was less carefully executed

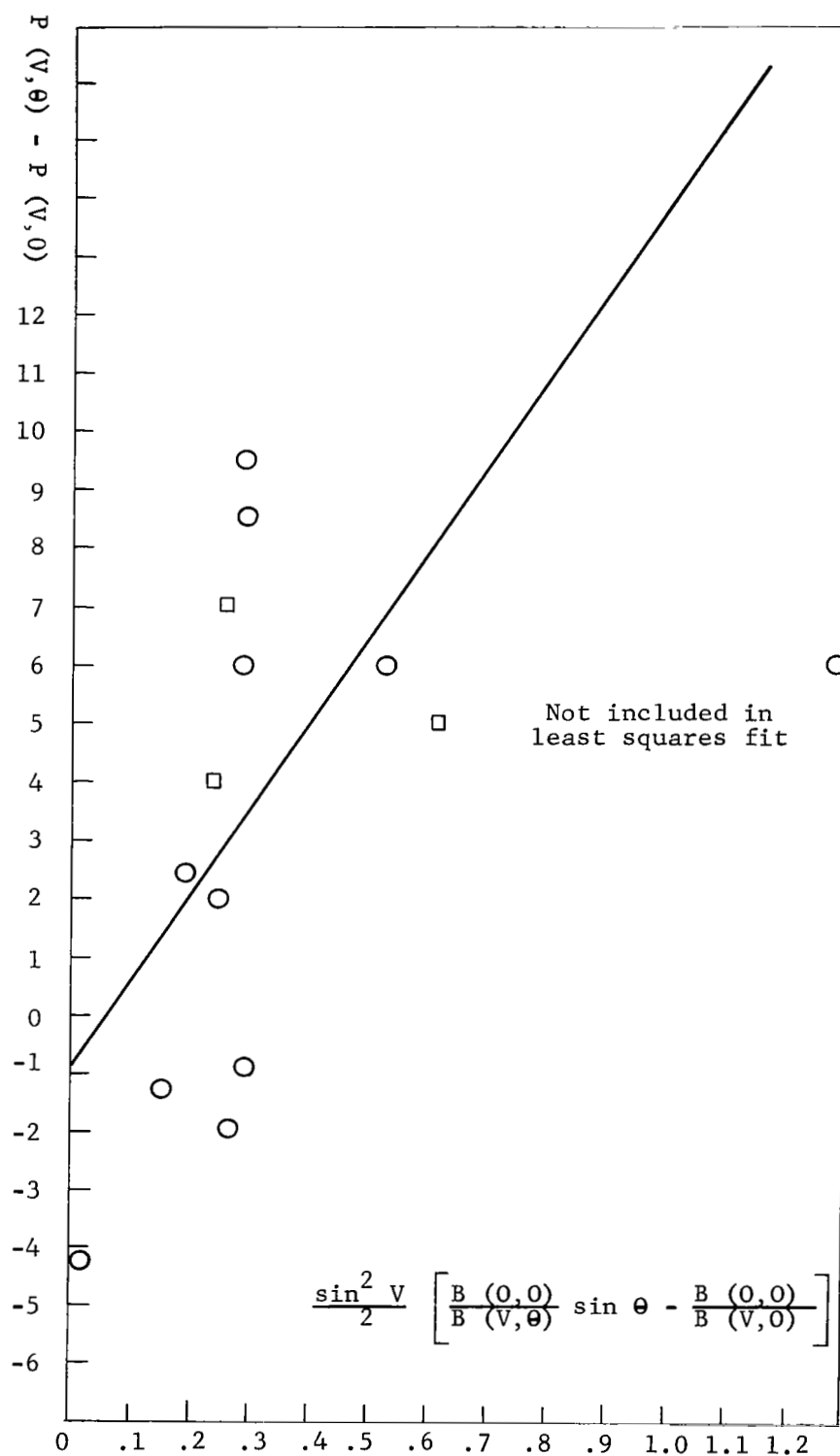


Fig. A-4 Plot of Data for Method 1 Using Photometric Data Correctly

than the first.

From the foregoing remarks, attaching an error to the result is not easy. Errors arising through use of the photometric data are greatest for measurements at large V because:

- 1) For $V > 30^\circ$ there is no published photometric curve and (see Fig. A-2) the extrapolation is rather uncertain.
- 2) Most measurements were made towards the terminator where the θ -dependence of the photometric curves is very strong. Hence, the results are very sensitive to the positions of these curves. Consequently, small errors in extrapolation have a large effect.

An example will demonstrate this fairly well. At $V = 30^\circ$ (using one of Dollfus' published curves) and $\theta = 55^\circ$ towards the terminator (a value used by Dollfus), an error of ± 0.05 in the photometric ratio gives $B(30,55)/B(0,0) = 0.32 \pm 0.05$, or an error of $\pm 15\%$. The scatter in the published data points²² range over ± 0.08 for these angles, so this is a reasonable estimate. For the $V = 40^\circ$ curve, a similar scatter would be expected for $\theta \sim 45^\circ$, but now the mean is a result of extrapolation, so that an error of twice this is not at all unlikely. A study of the published data²² leads to the conclusion that in this data reduction, the errors to be assigned due to uncertainties in the photometric data (or due to lack of such data) are

$0^\circ < V < 30^\circ$	$-60^\circ \leq \theta \leq +2.5^\circ$	$\pm 6\%$
$0^\circ < V < 30^\circ$	$\theta > +25^\circ$	$\pm 15\%$
$V > 30^\circ$	$\theta > +25^\circ$	$\pm 30\%$

For points very near the terminator the error is greater still. The derivations are fairly arbitrary of course because, for example, the position of the extrapolated curve for $V = 40^\circ$ is related to interpolations between the curves $V = 10^\circ, 20^\circ, 30^\circ$. They do serve, however, as an indication of the errors to be expected, although the errors near the sub-solar point are less than the indicated $\pm 8\%$; however, due to the nature of the polarimeter, polarimetric measurements at the sub-solar point (small θ) are much less accurate than at larger θ . In connection with these errors it is worth noting that in the second of the two estimates for B_a/B_s mentioned on page 11 the three points with $V > 40^\circ$ (for which $\theta < 55^\circ$) were included. Thus, it is seen that they do not change the result very much. It is assumed therefore, that an error of $\pm 15\%$ should be included in the estimate of (B_a/B_s) .

It is important to appreciate the assumptions made in a least squares fit to the data. The usual formulae were used, minimizing the vertical displacement of points from the line which implies that all the error lies in the ordinates. This was the basis for the lines drawn in Figures A-3 and A-4. Such a procedure requires justification by a proper assessment of the errors associated with the various quantities. When this is done, it appears that a more careful application of the least squares method would increase the slope of the line in Figure A-4 to some extent. It thus appears that $B_a/B_s = 0.015$ is probably a lower limit.

Dollfus used a finite spectral band width in his measurements. He indicated²¹ that the colored glass filters used for 0.61μ were similar to a Wratten filter 25A, and that this must be combined with the sensitivity curve for the eye. The result is a half-width of 500 \AA (approximately, since the profile has a longer tail in the red). The error in neglecting to integrate over this spectral profile does not appear in the deduction of B_a/B_s , providing a similar filter was used in the photometric measurements. These measurements were made by a polarimetric method, so that it is very probable that a similar filter was used. Errors due to measurement of θ could be either way, although there may be a systematic effect, and are assumed to be included in the estimated standard deviation of 0.007.

Adding the major errors now gives the standard error (δ)

$$\text{as } \left(\frac{\delta}{0.0147} \right)^2 = \left(\frac{0.0072}{0.0147} \right)^2 + (0.15)^2 ,$$

so

$$\frac{B_a}{B_s} = 0.0147 \pm 0.0100 .$$

This error is the best that can be obtained from the data but should be used with caution. There still remains the uncertain contribution from aerosol particles, for which no estimate can be made, and there may be other factors as yet unknown. The effect of errors in the least squares fit is also neglected in the above result.

Second Method

In this method Dollfus made measurements at $\theta = 0$ and $\lambda = 0.53\mu$ and 0.61μ . Referring to equation (5) it is seen that for this particular case it becomes

$$P(V, 0, \lambda_1) - P(V, 0, \lambda_o) = P_s(V, \lambda_1) - P_s(V, \lambda_o) + \frac{B_a}{B_s} \cdot \frac{B_o}{B_V} \cdot \frac{B_o}{B_\theta} \cdot \frac{\sin^2 V}{2} \left[\left(\frac{\lambda_o}{\lambda_1} \right)^4 \frac{1}{a(\lambda_1)} - 1 \right]. \quad (9)$$

In his work, Dollfus omitted the first two terms in the right-hand side, thus neglecting the variation of surface polarization with wavelength. Dollfus explained²¹ that he did this because at that time, there was no data which could be inserted into the equation. He was aware that this method produced only an approximate value for B_a/B_s but regarded this as a useful check on the first method. Consequently he also included measurements made on the dark areas of Mars. His results for B_a/B_s of 0.030 and 0.031 for the dark and bright areas respectively did provide such a check. In his data reduction Dollfus picked out one point for $P_{\lambda_1} - P_{\lambda_o}$ at a given angle. For the bright areas, the points are shown here in Figure A-5; the point taken by Dollfus was $V = 30^\circ$ $P = 0.007$. Such a procedure gives more weight to points around $V = 30^\circ$ than those at other V . This may be justified by some other knowledge, e.g. if $\{P_s(V, \lambda_1) - P_s(V, \lambda_o)\}$ was small at $V = 30^\circ$; there is no real evidence that this is the case. Replotting the data in straight line form (ΔP as ordinate) can give a slope of B_a/B_s . When this was done using the photometric data obtained from Dollfus⁶ the result gave (by least squares),

$$\frac{B_a}{B_s} = 0.0071 \pm 0.0044 ,$$

$$\text{Intercept} = 0.0059 \pm 0.0015,$$

whereas the intercept should be zero. This could be due to surface polarization effects. However, values for the wavelength

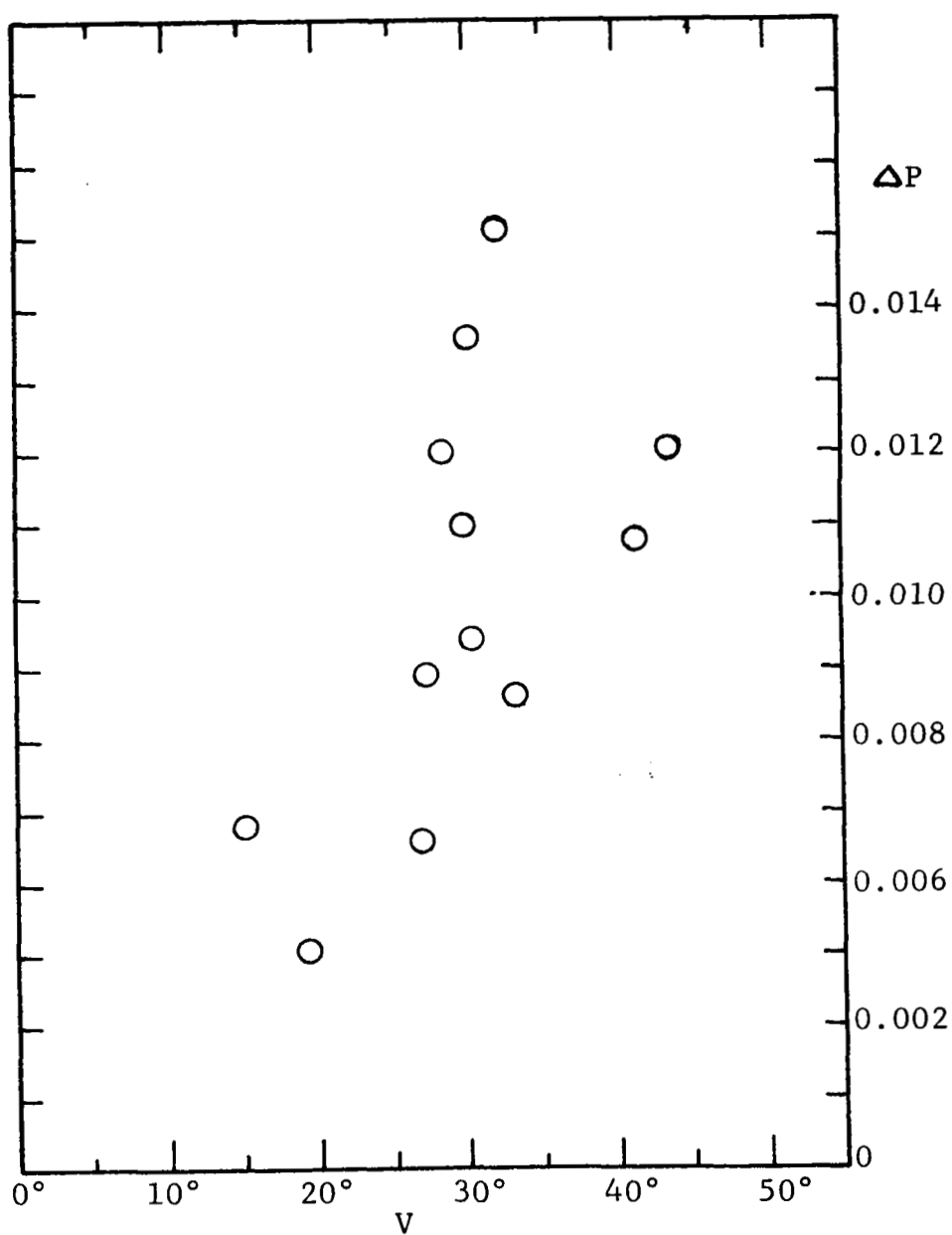


Fig. A-5 Reproduction of the data in Figure 48 of [6] for the bright regions of Mars only. This shows the difference in polarization (green-red) for $\theta = 0$.

dependence of polarization by limonite, supplied by Dollfus²¹, showed P_s to oscillate with V , varying between + 0.6 to -1.4 for $\lambda_1 = 0.55\mu$, $\lambda_0 = 0.63\lambda$ (see page 6). Coulson's data²⁴, which has already been mentioned in the main text, does show a variation in the polarization of his limonite sample. For the two wavelengths 0.64μ and 0.492μ , the polarizations at $V = 20^\circ$ were -18% and -20% respectively; for $V = 30^\circ$ the respective figures were -2% and +5%. These figures are quite different from those obtained from Dollfus' data²¹. This limonite sample, however, does not fit the Mars polarimetric profile and so the Dollfus sample (which presumably does fit) should be a better guide; but the effect is too uncertain to be included in the calculation.

The reason for this low value of B_a/B_s is not clear, but the result is much lower than the one originally given by Dollfus, namely $B_a/B_s = 0.031$, and supports the supposition that his original data reduction gave results which were too high. The uncertainties in this method exceed those of method 1 due to the introduction of wavelength dependences. Not only is there the uncertain behavior of the Martian surface in this respect, but also the atmosphere which is probably not a true Rayleigh scatterer. Thus the error given to the value of B_a/B_s shouldn't be taken literally, as the overall uncertainty probably exceeds $\pm 100\%$.

Third Method

This method is a combination of methods 1 and 2. The equation used by Dollfus is

$$(P_{\theta} - P_o)_{\lambda_1} - (P_{\theta} - P_o)_{\lambda_o} = \frac{B_a}{B_s} \frac{\sin^2 V}{2} \frac{B_o}{B_V} \left[\frac{B_o}{B_{\theta}} \sec \theta - 1 \right] \cdot \left[\frac{1}{a(\lambda_1)} \cdot \left(\frac{\lambda_o}{\lambda_1} \right)^4 - 1 \right]. \quad (10)$$

In this equation Dollfus has neglected the λ -variation of $\Delta(\theta)$. A check of Dollfus' calculation shows an arithmetical error, neglecting to subtract unity in the first bracket (first pointed out by Chamberlain and Hunt¹⁹).

Correcting for this error yields

$$\frac{B_a}{B_s} = 0.034, 0.0376, 0.0775.$$

Dollfus made only three data reductions by this method. In his papers^{5,6} he states that the third was the least accurate, and he later²¹ indicated that the atmospheric transparency was poorer at the time this measurement was made. Using the figures which Dollfus gives⁵ with the photometric curves mentioned earlier and the following equation,

$$(P_{\theta} - P_o)_{\lambda_1} - (P_{\theta} - P_o)_{\lambda_o} = \frac{B_a}{B_s} \cdot \frac{\sin^2 V}{2} \left[\frac{B(0,0)}{B(V,\theta)} \sin \theta - \frac{B(0,0)}{B(V,0)} \right] \cdot \left[a_{\lambda_1} \left(\frac{\lambda_o}{\lambda} \right)^4 - 1 \right], \quad (11)$$

one obtains,

$$\frac{B_a}{B_s} = 0.050, 0.016, 0.009,$$

respectively. It is interesting to note that the first measurement was made towards the limb and the last two towards the

terminator. In this method there are all the uncertainties associated with both methods 1 and 2 without a sufficient number of measurements to enable statistics to be used effectively. Therefore, the results must be weighted much lower than those of the first two methods.

Fourth Method

The fourth method is rather different from Dollfus' other two methods. He considers light from the whole planet and hence works in terms of intensity, not brightness. By a simple calculation he deduces that

$$I_a = 2\pi R^2 B_a,$$

and

$$I_s = \pi R^2 B_s,$$

where

$$\frac{B_a}{B_s} = 0.5 \frac{I_a}{I_s}.$$

There are complications due to the non-uniform brightness of the ground so he takes a factor 0.7 rather than 0.5, without any explanation. Light from occasional veils and clouds would be included in these intensities.

Dollfus attributes a low accuracy to this method which seems highly probable. Further, errors could not be placed upon the measurements and data reduction without a large effort which seems pointless. Hence this method was not analyzed, although Dollfus did obtain approximate agreement with his first three deductions.

Absorption

The effect of absorption is to raise the value of B_a/B_s . Opik's result would raise it by 50%. This is probably much too much (Dollfus²¹) and so, since no figure is available, only a wider error (or uncertainty) limit can be placed on the final result. It appears very probable that 20% on B_a/B_s would present an upper limit so this figure is used below in giving the final estimate for B_a/B_s .

Final Estimate for B_a/B_s —

Dollfus' first method is the most accurate. When the data is processed without assuming that the dependence on V and θ can be separated, a least squares fit to the data gives $B_a/B_s = 0.0147$.

2.3 The Meaning of the Error Attached to B_a/B_s

A note on the meaning of the error attached to B_a/B_s is in order. The mean squares determination gives the standard error. In normal error theory, the probability that the mean of a set of values lies within the standard error is 68%. The probability that it lies within twice the standard error is 95.4%; three times the standard error is 99.7% and so on. Consequently, in taking the standard error (page 15), there is only a 68% probability that the deduced value lies within these limits. The other two errors which were included, due to uncertainties in the photometric data (and its application through interpolation and extrapolation) and the effect of Martian atmospheric absorption, were not assessed statistically and therefore cannot be regarded in this way. Drawing a comparison one might estimate the following:

	<u>Photometry</u>	<u>Absorption</u>
68% probability	$\pm 10\%$	+ 15%
95% probability	$\pm 20\%$	+ 30%

These figures are rather intuitive but will result in a closer correlation with the least squares error. Consequently one now obtains the following results;

$$\frac{B_a}{B_s} = 0.015 \pm \begin{matrix} 0.010 \\ 0.007 \end{matrix} \quad \text{68\% probability,}$$

and

$$\frac{B_a}{B_s} = 0.015 \pm 0.020 \quad 95\% \text{ probability .}$$

In regarding these error limits one should still bear in mind the point already mentioned several times in this report; namely, that the conclusions of this evaluation could be upset by better knowledge of the Mars atmosphere.

2.4 The Blue Haze and Atmospheric Extinction

Introduction

In order to gain an understanding of the kinds of particles which might be present in the Martian atmosphere, a review of the observational evidence pertaining to this question has been made. In the course of this review, it became apparent that, in many cases, the observations have been somewhat over-interpreted, and it is the interpretations which are commonly referred to rather than the evidence. Consequently, an attempt was made to examine the interpretations as well. This led to the production of a document which was considerably longer than we originally intended. It is fairly obvious that more observational and theoretical work needs to be done before great confidence can be placed in our knowledge of the nature of particulate matter in the Martian atmosphere. Here we shall simply present a brief summary of the relevant observational evidence and the conclusions of the complete review.

Observations

A range of cloud phenomena has been observed in the Martian atmosphere^{1,62}. These include; yellow clouds, attributed to violent dust storms; white clouds and blue clouds. The white clouds are usually diffuse, of low contrast, and cover large areas, especially at the sunrise terminator. The blue clouds

are small and sharp, moving with the surface features as the planet rotates. In addition, small white clouds, or patches, have also been described^{63,64}. Photographic observations made over a range of wavelengths show an obscuration of detail in the blue and ultraviolet, which is given the name Blue Haze. A graphic illustration of this obscuration is given by de Vaucouleurs¹. In Plate III of his book, he shows a series of nearly simultaneous photographs taken by Wright at six effective wavelengths ranging from 0.37μ to 0.76μ . From these photographs, it appears that there is some loss of contrast even in the red (compared with the infrared); however this becomes quite perceptible in the yellow and is complete in the violet (see also Slipher⁶⁵ Plate XV). As the wavelength of the light decreases, the pole caps become more prominent as do the blue clouds; the photographs by Wright show the planet to have a mottled appearance in the blue and ultraviolet. This non-uniformity is usually found; but not always. Slipher⁶⁵ gives photographs which do not show these cloud features, e.g., Plates VII, XXIII, XXIV; his Plate XXIII shows twenty photographs of Mars taken in blue light which serve to emphasize the patchy appearance that usually prevails. It is interesting to note, in these last plates, that sometimes the pole caps appear small and bright, while at other times they are large and diffuse.

Blue clearing is a phenomenon which has aroused much interest. The phenomenon may be described as a dispersal of the obscuring haze so that surface features may be discerned

in the blue. Many instances of blue clearing have been reported, mostly at opposition. Since observations on Mars are usually made at opposition, this is not necessarily significant. Slipher has made a survey of plates taken in blue light between 1922 and 1960, studying some 60,000 photographs. He found that the observational evidence tends to support the conclusion that there is a definite tendency for pronounced blue clearing to occur near opposition, although the study did disclose examples of blue clearing as far as 60 days from opposition. Sagan and Kellogg⁶⁶, commenting on this survey, point out that the results are subject to observational selection and that it is not clear whether any correlation with opposition will remain when the effects of such selection are removed. Slipher points out that, at opposition, the observers' line of sight is nearly parallel to the Sun's rays and under these conditions greater contrast may be observed; Menzel⁷¹ also suggests this as an interpretation of blue clearing.

At this point, it is worth commenting on the nature of the observed blue clearings. Very few of these give comparable photographs in the blue and red; examples that do are the oppositions of 1926, 1937, 1941, 1954, for which Slipher⁶⁵ shows photographs. For the 1937 example he shows photographs taken in the yellow and the blue in which the correlation is unmistakable; however, the contrast in the blue is still inferior to that in the yellow (one should bear in mind that these comments are made on published reproductions which are obviously inferior to the original plates. In addition, the plate characteristics

are probably different for the two spectral regions.) As Hess²⁷ has pointed out this is not necessarily due to particulate matter because, since the bright areas are red, a decrease in contrast is to be expected at shorter wavelengths (and this was the early explanation of the "obscuration" in the blue). In the majority of published photographs, blue clearing is only slight, the contrast is low and surface features can only be discerned in certain regions of the planetary disk. Since photographs of the blue haze often show many features which are of atmospheric origin it is obvious that great care has to be taken to insure that a partial clearing is, in fact, being observed.

Attempts to define an effective wavelength cut-off for the blue haze have led to a figure of $\lambda \sim 0.54\mu$. Slipher⁶⁵ used a combination of spectrographic plates and Wratten filters and obtained results which suggested that the obscuration was not gradual but was more or less abrupt at $\lambda = 0.455\mu$. Richardson⁶⁷ reports that six independent eye estimates on spectrograms covering the region $\lambda = 0.400\mu$ to 0.500μ gave the wavelength at which the maria became indistinguishable in the range 0.426μ to 0.458μ with a mean of 0.442μ ; the maria could be followed with uncertainty down to 0.460μ . When a blue clearing is observed there seems to be no evidence to show whether this cut-off is simply extended to a slightly lower wavelength or whether there is a general clearing to much lower wavelengths. Opik⁷⁰ estimates that blue clearing is confined to the blue and that in the

violet a permanent veil covers the planet, presumably not clearing. Kuiper⁴⁹ also supports this view. There certainly does not appear to be any photographic evidence in the ultraviolet which indicates the dispersion of the haze, suggesting that a blue clearing might be a short of the cut-off to slightly lower wavelength.

Conclusions

The observational evidence is convincing in suggesting that particulate matter is frequently present in the Martian atmosphere in appreciable quantities. Dollfus has stated that the observations he made to determine the Martian surface pressure were obtained at times when the atmosphere of the planet appeared particularly transparent. This precaution would eliminate effects due to the yellow clouds or dust storms but it seems likely that very small particles carried aloft in these storms would always be present - in analogy to the condensation nuclei in the Earth's atmosphere. In addition, there is the problem posed by the blue haze. Dollfus does not state whether his observations were made at times of blue clearing. Even if this were the case, however, there appears to be evidence that the clearing is simply a decrease in the wavelength of the blue haze cut-off. Thus, whatever agent is responsible for the haze remains in the atmosphere and will consequently affect the polarimetric observations.

No one theory of the blue haze explains the several features of this phenomenon. Soviet observers believe that the obscuration can be explained entirely by scattering, but fail to indicate how the albedo can be so low. For the most part, they emphasize Rayleigh scattering; although some mention is made of other scatterers, they do not appear to have made any calculations similar to Kuiper's⁷, nor to have made estimates of the size distributions of particulate scatterers.

Kuiper^{7,14} also proposes that the haze is caused by scattering but suggests a very low surface albedo to account for the low total albedo of the planet. An obvious test of this point would be a determination of planetary albedo during a period of blue clearing. It is interesting to note in passing that the moon has an ultraviolet albedo only slightly greater than that of Mars; 0.066 vs. 0.052. The moon, of course, has no atmosphere to contribute to this low value. The presence of a pure molecular atmosphere on the moon would lead to an increase in the albedo due to Rayleigh scattering.

Several alternative theories have been proposed, but it appears that the only ones which are tenable are those which require true atmospheric absorption as well as scattering. Pure absorption explains the low albedo, but has other difficulties. The work of Kuiper^{7,14}, Hess⁶⁸, Goody⁶⁹ and others, points to the scattering by H₂O ice or CO₂ ice crystals, almost certainly the former, which offers a plausible explanation for the rapid clearings that are obtained; namely, by sublimation

of the particles. A pure scattering layer would increase the albedo in the blue, but such an increase would be reduced by the assumed absorption which, to avoid limb darkening, must not be above the scattering layer. Limb darkening is sometimes observed, but usually not; although some photographs show brightening followed by darkening at the extreme limb, which can be interpreted (following Harris²⁸) by a judicious combination of scattering and absorption. One problem with absorption theories is the specification of the nature of the absorber, for which no convincing suggestion has been put forward. Ice crystals do not absorb at the required wavelength. Absorption by molecular species has been suggested, but not observationally confirmed. This is also the case for a smoke made up of carbon particles.

The work of Soviet astronomers has been directed towards making estimates of the extinction coefficients of the Martian atmosphere. Öpik⁷⁰ has also worked in this field, using Soviet experimental data. These results show that there may be continuous absorption from the red to the blue, not just in the blue. This absorption could be due to particulate scattering rather than true absorption, however, and separation of the two is somewhat suspect in Soviet work because of the assumptions in their theory. This is true in Öpik's work as well, but to a lesser extent.

The pure absorption theory has other difficulties besides the specification of the absorbing substance. The rapid clearing that is observed at times would be hard to account for

if this required the removal of the absorbing layer - a correlation of clearings with opposition is improbable. Also pure absorption can only produce a darkening, not a loss in contrast (Hess²⁷). The relatively sharp cut-off at 0.450μ is also difficult to explain. Kuiper's theory also has difficulty with the sharp cut-off in the blue; but, on the other hand, readily explains rapid blue clearing.

Dollfus, Focas⁷⁸ and co-workers believe that the loss of visible detail in the blue is primarily due to the low surface contrast at these wavelengths, there being only a small amount of atmospheric aerosol matter. The so-called blue clearings are then attributed to the selective formation of clouds over the light areas. Dollfus²¹ has recently made measurements on the albedo at the pole caps at various wavelengths and, although the data has not yet been properly reduced, believes the absorption to be small, certainly much less than that proposed by Öpik.

Kellogg and Sagan⁷¹ have suggested that it is possible to fit a model to the surface and atmosphere of Mars unambiguously by mapping the intensity and polarization from various parts of the disk at several wavelengths. This suggestion refers to a report by Sekera and Vieze describing various model atmospheres to which the data would be matched, thus obtaining the correct atmosphere. The work would best be accomplished from a space probe to obtain the necessary high angular resolution.

Kuiper¹⁴ discusses similar ideas in relation to work in the UV, and refers to Gehrels' and Teska's⁷⁹ UV polarization measurements.

Whatever possible combination of scattering and absorption is responsible for the blue haze, the presence of this phenomenon will have a definite effect on the polarimetric observations. The presence of absorption will lead to an underestimate of surface pressure if the absorption extends to longer wavelengths. Scattering particles will have the reverse effect. A combination of the two will produce intermediate results which will probably be wavelength-dependent.

2.5 The Determination of Surface Pressure from

$$\frac{B_a^\circ}{B_s^\circ}$$

The basic technique used by Dollfus⁵ in his determination of the Martian surface pressure involves the separation of the total brightness of the planet into a surface component and an atmospheric component. This separation arises from differences in the polarizing properties of the two sources. A number of assumptions as to the composition and scattering properties of both the atmosphere and surface are made, and several important sources of brightness such as particulate scattering and forward scattering of surface reflected radiation are neglected.

The separation of the surface and atmospheric contributions results in a determination of B_a°/B_s° ; the ratio of the atmospheric brightness in the center of the disk of the surface brightness in the center of the disk. Since the visible surface brightness is much greater than the visible atmospheric brightness, Dollfus takes the total brightness of the planet, determined from independent photometric observations, as equal to the surface brightness B_s and obtains an absolute value of B_a° from the ratio B_a°/B_s° . Then, assuming that the entire atmospheric brightness is due to Rayleigh scattering by an atmosphere possessing the same scattering and polarizing properties as air, he applies simple

Rayleigh scattering theory to yield the number of molecules per cm^2 -column, in the center of the disk, required to produce the atmospheric brightness B_a° . This value and the gravitational acceleration on Mars yield the surface pressure directly.

The pressure obtained in the above manner is necessarily only an estimate, since other contributions to B_a° , such as particle scattering, will yield lower pressure estimates in the absence of absorption. Dollfus⁵, in his original work states that his result is intended only as "an order of magnitude estimate".

The following is a reproduction of Dollfus' derivation of surface pressure using more recent values of both B_a°/B_s° and photometric constants^{28,61}. The corresponding results obtained by Dollfus⁵ are shown in closed brackets for comparison.

The brightness B_a° of an atmosphere of thickness h (cm), in the center of the disk, subjected to illumination E is given by

$$B_a^\circ = R.E. h \left(1 + \frac{1 - \rho}{1 + \rho} \cos^2 V \right),$$

where ρ is the depolarization factor of the gas and V is the phase angle. At opposition, $V = 0$, so that

$$B_a^\circ = \frac{2}{1 + \rho} R.E. h, \quad \boxed{B_a^\circ \sim 2 R.E. h}$$

where R is the Rayleigh scattering constant⁸⁰,

$$R = \frac{\pi^2 (\mu^2 - 1)^2}{2 n \lambda^4} - \frac{6 (1 + \rho)}{(6 - 7\rho)}$$

$$R = \frac{\pi^2 (\mu^2 - 1)}{2 n \lambda^4} \frac{6 (1 + \rho)}{(6 - 7\rho)}$$

The discrepancy in the term $(\mu^2 - 1)^2$ appears to be a typographical error.

in which⁸¹,

μ = refractive index of air = 1.000293

λ = wavelength = 6200 Å,*

n = molecules per cm³ = 2.687 x 10¹⁹,

ρ = depolarization factor for air = 0.035.

μ = 1.00029

λ = 6200 Å

n = 2.9 x 10¹⁹

ρ = 0.04

Thus

$$R = 4.29 \times 10^{-9} \text{ cm}^{-1}/\text{ster},$$

$$R = 4.2 \times 10^{-9} \text{ cm}^{-1}/\text{ster}$$

and the brightness B_a° becomes

$$B_a^\circ = 8.28 \times 10^{-9} \text{ E. h stilb.}$$

$$B_a^\circ = 8.4 \times 10^{-9} \text{ E. h stilb}$$

The illumination from the Sun at 1 AU is 13.5 phots⁶¹ so that at the orbit of Mars (1.52 AU from the Sun) the illumination is

$$E = \frac{13.5}{(1.52)^2} = 5.85 \text{ phots}$$

and the atmospheric brightness becomes

$$B_a^\circ = 4.84 \times 10^{-8} \text{ h (cm) stilb.}$$

Using the corrected value of $B_a^\circ/B_s^\circ = 0.015$ (see Section 2.2 of text) and other photometric data⁵ which gives the ratio of the brightness of the center of the disk B_s° to that of the entire disk B_s as

$$\frac{B_s^\circ}{B_s} = \frac{0.35}{0.31} = 1.13 ,$$

* Although Dollfus refers to a wavelength of 6100 Å in his papers, he employed a wavelength of 6200 Å in his calculations as in his work on the planet Mercury. Because of the wide bandwidths of the filters employed, this difference is not felt to be significant, and the calculations in this report consider the value of 6200 Å.

we have

$$B_a^\circ = 0.015 B_s^\circ = (0.015)(1.13) B_s = 4.84 \times 10^{-8} h \text{ (cm) stilb,}$$

so the equivalent thickness of the Martian atmosphere is,

$$h \text{ (km)} = 3.50 B_s (6200 \text{ \AA}) \text{ stilb}$$

where $B_s (6200 \text{ \AA})$ is the brightness, in stilbs, of the disk of Mars at 6200 \AA at opposition. The value of $B_s (6200 \text{ \AA})$ is determined photometrically as follows:

Harris²⁸ gives the visual magnitude of Mars, corrected for absorption in the Earth's atmosphere, as

$$M_{\text{♂}} = -2.01 .$$

Since a star of magnitude $M = 0$, outside the atmosphere, corresponds to $2.65 \times 10^{-10} \text{ lumens/cm}^2$, we have the intensity of $M_{\text{♂}} = -2.01$ as $L_{\text{♂}}$ where

$$2.01 = 2.5 \log \frac{L_{\text{♂}}}{2.65 \times 10^{-10}} ,$$

or

$$L_{\text{♂}} = 1.69 \times 10^{-9} \text{ lumens/cm}^2 .$$

In opposition, the solid angle ω subtended by Mars from the Earth (Mars-Earth distance = 0.52 AU) is⁶¹

$$\omega = 6.04 \times 10^{-9} \text{ ster} ,$$

and the brightness B_s of the Martian disk is

$$B_s = \frac{L_{\text{♂}}}{\omega} = \frac{1.69 \times 10^{-9}}{6.04 \times 10^{-9}} = 0.28 \text{ stilbs,}$$

Dollfus uses the older definition in which 1 lux corresponds to $M_v = -14.3$ to obtain $B_s = 0.24 \text{ stilb}$:

where $B_s = B_s (5500 \text{ \AA})$ for the visual magnitude.

For 6200 Å this becomes

$$B_s (6200 \text{ Å}) = B_s (5500 \text{ Å}) \frac{p (6200 \text{ Å})}{p (5500 \text{ Å})},$$

Dollfus transfers B_a° by $(\lambda/\lambda_0)^4$ which introduces error since $R = R(\lambda, \mu)$ and $\mu = \mu(\lambda)$.

where $p(\lambda)$ is the monochromatic albedo of the disk. de Vaucouleurs⁸² gives $p(5500 \text{ Å}) = 0.16$ and $p(6200 \text{ Å}) = 0.21$ so that,

$$B_s (6200 \text{ Å}) = 0.28 \left(\frac{0.21}{0.16} \right) = 0.368 \text{ stilb.}$$

The equivalent thickness of the Martian atmosphere, for $B_a^\circ/B_s^\circ = 0.015$, is then

$$h_{\sigma} (\text{km}) = 3.50 \times 0.368 = 1.29 \text{ km.}$$

$$h_{\sigma} = 1.9 \text{ km for } B_a^\circ/B_s^\circ = 0.028$$

The thickness h_{\oplus} of the Earth's atmosphere is 7.99 km and the surface pressure P_{\oplus} is 1013 mb. The gravitational pull g_{σ} on Mars is 376 cm sec^{-2} and that of the Earth is $g_{\oplus} = 980 \text{ cm sec}^{-2}$.

Thus the Martian pressure $P_{\sigma} = P_{\oplus} \frac{g_{\sigma} h_{\sigma}}{g_{\oplus} h_{\oplus}}$ is equal to

$$P_{\sigma} = 1013 \times \frac{376}{980} \times \frac{1.29}{7.99} = 63 \text{ mb}$$

$$P_{\sigma} = 90 \text{ mb for } B_a^\circ/B_s^\circ = 0.028$$

Alternate Technique

For comparison, we have formulated the problem in a slightly different manner.

The brightness, in opposition, of an atmosphere of thickness h containing n molecules per cm^3 is

$$B_a^\circ = E \sigma (nh) \frac{p(\cos 0)}{4\pi}$$

where σ is the Rayleigh scattering coefficient per molecule and $p(\cos 0) = 1.5$ is the Rayleigh phase function for backscatter.

Allen⁶¹ gives

$$\sigma = \frac{128 \pi^5}{3 \lambda^4} \alpha^2 ,$$

where α is the polarizability of the gas. The pressure, which is just the weight of the molecules above a unit area, can be written

$$P = \frac{(nh) M g}{A_0} ,$$

where M is the gram molecular weight of the gas, g is the gravitational acceleration on Mars and A_0 is Avogadro's number. Thus,

$$P = \frac{B_a^\circ M g 4 \pi}{E \sigma A_0 p(\cos \theta)} .$$

We can write B_a° in the form

$$B_a^\circ = \left(\frac{B_a^\circ}{B_s^\circ}\right) \left(\frac{B_s^\circ}{B_s}\right) B_s ,$$

where (B_a°/B_s°) is the ratio determined from the polarization, (B_s°/B_s) is the photometric brightness ratio of the center to the disk and B_s is the brightness of the disk determined photometrically. By the definition of \bar{p} , the geometrical albedo,⁸¹

$$B_s = \bar{p} \frac{E}{\pi} ,$$

and the pressure can be written as

$$P = \left(\frac{B_a^\circ}{B_s^\circ}\right) \left(\frac{B_s^\circ}{B_s}\right) \frac{4 \bar{p} M g}{\sigma A_0 p(\cos \theta)} \left\{ \begin{array}{l} \text{Note that the solar flux no} \\ \text{longer enters the expression.} \end{array} \right.$$

For 6200 \AA , Allen⁶¹ gives $\sigma(\text{CO}_2) = 6.17 \times 10^{-27} \text{ cm}^2$,
 $\sigma(\text{N}_2) = 2.72 \times 10^{-27} \text{ cm}^2$ and $\sigma(\text{air}) = 2.64 \times 10^{-27} \text{ cm}^2$. With

the above values for (B_a°/B_s°) , (B_s°/B_s) , \bar{p} , M , g , $p(\cos \theta)$ and A_o , this gives:

$$P = 5.9 \times 10^{-27} \frac{M}{\bar{G}} (\text{mb})$$

and for the gases considered we have

$$P (\text{air}) = 64.5 \text{ mb}$$

$$P (\text{CO}_2) = 42 \text{ mb}$$

$$P (\text{N}_2) = 61.5 \text{ mb}$$

These results are essentially in agreement with those of Dollfus but the technique more readily lends itself to calculation.

For a mixture of two gases in proportion x of gas 1 to $(1-x)$ of gas 2, the pressure is given by

$$P = \left(\frac{B_a^\circ}{B_s^\circ} \right) \left(\frac{B_s^\circ}{B_s} \right) \frac{4 \bar{p} g}{A_o p (\cos \theta)} \left[\frac{x M_1 + (1-x) M_2}{x \bar{G}_1 + (1-x) \bar{G}_2} \right],$$

and for an atmosphere of $1/3 \text{ CO}_2$ and $2/3 \text{ N}_2$ the pressure is equal to

$$P (1/3 \text{ CO}_2 + 2/3 \text{ N}_2) = 51 \text{ mb}.$$

2.6 Musman's Upper Limit to a Rayleigh Scattering Atmosphere on Mars

If, in the absence of absorption, one assumes that the entire brightness of a planet is due to Rayleigh scattering of sunlight by the molecular atmospheric constituents, then the optical thickness of atmosphere required to produce this brightness will necessarily be an upper limit as will the corresponding pressure. In the UV, where the surface albedo is low, this upper limit may be a good estimate. Musman¹⁸ matched the measured UV reflectivity of Mars with calculated models of a Rayleigh atmosphere and obtained an optical thickness of 0.058 at 3300 Å. The following is an attempt to reproduce Musman's work by matching the measured reflectivity with Rayleigh atmospheric models calculated by Coulson⁸³.

Reproduction of Musman's Work

G. de Vaucouleurs⁸⁴ measured the magnitude of Mars photometrically at 3300 Å on 23 October 1958 ($\alpha = 21^\circ$) and obtained a magnitude difference $m_\odot - m_\text{Mars} = -26.93$ when reduced to unit distance from the Earth and Sun. Allen⁶¹ (p. 144) gives the dimensionless reflectivity $p_\varnothing(\alpha)$ of a planet as:

$$\log p_\varnothing(\alpha) = 0.4 (m_\odot - m_\text{Mars}) + 2 \log (r \Delta / R) .$$

For Mars as above; $r \Delta = 1$ and $R^{-1} = (206,265/4.68) = 4.4 \times 10^4$.

$$\begin{aligned}\text{Thus, } \log p \phi (21^\circ) &= (0.4)(-26.93) + 2 \log (4.4 \times 10^4) \\ &= -10.77 + 8 + 1.287 = -1.485\end{aligned}$$

$$\text{or } p \phi (21^\circ) = 0.0327$$

For a perfectly reflecting Lambert sphere, in opposition, the Bond albedo $A = p_o q = 1$ and $q = 1.5$, thus $p = 2/3$. The illumination from the planet is proportional to the area illuminated $\left[\phi(\alpha) = \frac{1}{2} (1 + \cos \alpha) \right]$, so for a phase angle $\alpha = 21^\circ$ we have $\phi(21^\circ) = 0.9688$ and $p_o \phi(21^\circ) = \frac{2}{3} (.9688) = .645$. Thus the reflectivity of Mars is only $\frac{0.0327}{0.645} (100) = 5.06\%$ that of a perfectly reflecting Lambert surface. Coulson⁸³ gives the reflectance (Bond albedo) of a planar model of the Earth's atmosphere (with a completely absorbing surface) as $A = 0.305$ at 3300 \AA for normal incidence. The Rayleigh scattering cross section for air is given by Allen⁶¹ (p. 88) as

$$\sigma^{air}(3300 \text{ \AA}) = 3.54 \times 10^{-26} \text{ cm}^2.$$

The molecular weight of air is $M = 28.966 \text{ gm mole}^{-1}$ so that unit optical thickness corresponds to

$$N = \frac{M}{\sigma A_o} = \frac{28.966}{(3.54 \times 10^{-26})(6.02 \times 10^{23})} = 1.36 \times 10^3 \text{ gm/cm}^2$$

of air at 3300 \AA where A_o is Avogadro's number. The optical thickness of the Earth's atmosphere at 3300 \AA is then

$$\tau_{Earth}^{3300 \text{ \AA}} = \frac{P \text{ (dyne cm}^{-2}\text{)}}{N \text{ (gm cm}^{-2}\text{)} g \text{ (cm sec}^{-2}\text{)}} = \frac{1.013 \times 10^6}{(1.36 \times 10^3)(.98 \times 10^3)} = 0.762.$$

Thus, the Bond albedo for an atmosphere of optical thickness

τ of air at 3300 \AA is:

$$A = \frac{0.305}{0.762} = 0.400 \tau .$$

The Bond albedo is $A = pq$ where q is a factor which represents the phase law. For a Lambert surface (perfect diffuser) $q = 1.5$ and the dimensionless reflectivity p , for optical thickness of air at 3300 \AA , is

$$p = \frac{A}{q} = \frac{0.400}{1.5} \tau = 0.267 \tau .$$

Thus, for an atmosphere with reflectivity $p = 0.0327$ at 3300 \AA , we require

$$\tau = \frac{p}{0.267} = \frac{0.0327}{0.267} = 0.1225 .$$

Coulson's treatment⁸³, however, is for an infinite (horizontally) plane parallel atmosphere.

If we consider a curved atmosphere of thickness h surrounding a planet of radius r which is illuminated by parallel light, the effective thickness h' of atmosphere (assuming the atmosphere to be optically thin) is given by

$$h' = \frac{2}{3} h \left\{ \frac{1 + 3x + 3x^2 + (2x + 1)^{3/2}}{(1 + x)^2} \right\} ,$$

where $x = r/h$ is the ratio of the planet's radius to the normal atmospheric thickness, and h' is the normal thickness which the same volume of planar atmosphere could occupy over a disk of radius r . Taking $x = 200$ we have $h' = 2.12$. Thus a planar atmosphere 2.12 times the normal thickness of a spherical atmosphere around a planet of the same diameter is required to produce the same intensity of scattered light. The normal

optical thickness of the Martian atmosphere is then

$$\tau = \frac{0.1225}{2.12} = 0.058$$

which is in agreement with the value derived by Musman¹⁸. Coulson²⁴ feels that this extrapolation of his data to a spherical atmosphere is an oversimplification of the problem because of the optical thickness of the Martian atmosphere in the ultraviolet.

The Rayleigh scattering coefficients per molecule at 3300 Å and the molecular weights of air, N₂, CO₂ and Ar at 3300 Å are⁶¹

$$\sigma \text{ (air)} = 3.54 \times 10^{-26} \text{ cm}^2, \quad M = 28.966$$

$$\sigma \text{ (N}_2\text{)} = 3.74 \times 10^{-26} \text{ cm}^2, \quad M = 28.00$$

$$\sigma \text{ (CO}_2\text{)} = 8.43 \times 10^{-26} \text{ cm}^2, \quad M = 44.00$$

$$\sigma \text{ (Ar)} = 3.34 \times 10^{-26} \text{ cm}^2, \quad M = 40.00$$

The amounts ($N = \frac{M}{\sigma \text{ Å}_0}$) of each gas required to produce unit optical thickness at 3300 Å are therefore,

$$N \text{ (air)} = 1.36 \times 10^3 \text{ g/cm}^2$$

$$N \text{ (N}_2\text{)} = 1.24 \times 10^3 \text{ g/cm}^2$$

$$N \text{ (CO}_2\text{)} = 0.87 \times 10^3 \text{ g/cm}^2$$

$$N \text{ (Ar)} = 1.99 \times 10^3 \text{ g/cm}^2 .$$

The pressure on Mars will then be $P \text{ (mb)} = Ng \tau = 2.18 \times 10^{-2} N \text{ (mb)}$ if only molecular Rayleigh scattering is involved. For the above species,

$$P (\text{air}) = 29.6 \text{ mb}$$

$$P (\text{N}_2) = 27 \text{ mb}$$

$$P (\text{CO}_2) = 19 \text{ mb}$$

$$P (\text{Ar}) = 43.5 \text{ mb}$$

For an atmosphere of $1/3 \text{ CO}_2$ plus $2/3 \text{ N}_2$ the pressure would be given by

$$P = \frac{g \tau}{A_o} \left[\frac{\frac{1}{3} M (\text{CO}_2) + \frac{2}{3} M (\text{N}_2)}{\frac{1}{3} \sigma (\text{CO}_2) + \frac{2}{3} \sigma (\text{N}_2)} \right] = 21.7 \text{ mb} .$$

The optical thickness $\tau = 0.058$ is an upper limit if no absorption takes place since the inclusion of either surface reflection or scattering particles would contribute to the observed brightness.

Alternate Technique

The geometric albedo⁸⁵ \bar{p} is the ratio of the average brightness of a planet B_m at full phase to that of a perfectly diffusing surface B_L at the same distance from the Sun and normal to the incident radiation

Assuming the surface albedo to be zero, the brightness of the planet is equal to the brightness of its atmosphere. The brightness, in opposition, of a plane parallel atmosphere of thickness h' containing n molecules per cm^3 and illuminated by flux E is

$$B'_m = E \sigma n h' \frac{p(\cos 0)}{4 \pi} ,$$

where σ = Rayleigh scattering cross section per molecule, and

$p(\cos 0) = \text{Rayleigh phase function for zero phase angle} = 1.5$.
 A spherical atmosphere of normal thickness h about Mars produces the same scattering as a parallel atmosphere of thickness $h' = 2.12 h$ (see above). Thus the brightness in opposition $[p(\cos 0) = 1.5]$ is

$$B_m = E \sigma n (2.12 h) \frac{(1.5)}{4\pi} .$$

The brightness of a perfectly diffusing surface illuminated by flux E normal to the surface is, by definition⁸⁵,

$$B_L = \frac{E}{\pi} .$$

The geometric albedo can then be written as

$$p = \frac{B_m}{B_L} = 0.794 \sigma n h .$$

The surface pressure on Mars resulting from nh molecules of molecular weight M per cm^2 -column is

$$P \left(\frac{\text{dyne}}{\text{cm}^2} \right) = \frac{n h M g_{\text{Mars}}}{A_0} = \frac{\bar{p} M g_{\text{Mars}}}{0.794 A_0} ,$$

where A_0 is Avogadro's number and g_{Mars} is the gravitational acceleration on Mars = 376 cm sec^{-2} . G. de Vaucouleurs⁸⁵ gives the geometric albedo of Mars at 3300 \AA as $\bar{p} = 0.045$ so the pressure can be written as

$$P \left(\frac{\text{dyne}}{\text{cm}^2} \right) = \frac{(0.045)(376)}{(0.794)(6.02 \times 10^{23})} \frac{M}{0}$$

or

$$P \text{ (mb)} = 3.54 \times 10^{-26} \frac{M}{\sigma} .$$

For CO_2 , $M = 44 \text{ gm mole}^{-1}$ and $\sigma = 8.43 \times 10^{-26} \text{ cm}^2$ while for N_2 , $M = 28 \text{ gm mole}^{-1}$ and $\sigma = 3.74 \times 10^{-26} \text{ cm}^2$. The corresponding surface pressures are,

$$P (\text{CO}_2) = 18.7$$

and

$$P (\text{N}_2) = 26.6$$

which are in good agreement with the values $P (\text{CO}_2) = 19 \text{ mb}$ and $P (\text{N}_2) = 27 \text{ mb}$ obtained by Musman.

2.7 The Effect of Particle Scattering on Visible Pressure Determinations

The atmospheric brightness, in opposition, at the center of a planetary disk due to simple Rayleigh scattering from two molecular constituents is

$$B_m^\circ = E \cdot h \cdot \frac{p(\cos 0)}{4\pi} (n_1 \sigma_1^v + n_2 \sigma_2^v),$$

where

E is the incident solar flux,

h is the atmospheric thickness,

$p(\cos 0)$ is the Rayleigh phase function for opposition = 1.5,

n_1, n_2 are the number of molecules of each species per unit volume, and

σ_1^v, σ_2^v are the Rayleigh scattering coefficients per molecule for each species in the visible (6200 Å).

The atmospheric brightness at the center of the disk due to particulate scattering is³², in opposition,

$$B_p^\circ = \frac{E \lambda_v^2}{8\pi^2} \mathcal{N} i_o^v,$$

where

λ_v is the wavelength of scattered radiation (6200 Å),

\mathcal{N} is the number of particulate scatterers per cm²-column, and

i_o^v is the Mie scattering coefficient for the particles in the visible (6200 Å) for backscatter.

The surface pressure is given by

$$P = \frac{hg}{A_o} (n_1 M_1 + n_2 M_2) ,$$

where M_1, M_2 are the gram molecular weights of the two atmospheric constituents. The pressure can thus be written

$$P = \frac{4\pi g}{A_o p (\cos \theta)} E \left[\frac{x M_1 + (1-x) M_2}{x \sigma_1^v + (1-x) \sigma_2^v} \right] B_m^o ,$$

when the gases are mixed in proportion x molecules of gas 1 to $(1-x)$ molecules of gas 2.

The observed atmospheric brightness B_a^o in the center of the disk can be expressed as

$$B_a^o = B_m^o + B_p^o = (B_a^o/B_s^o)^v (B_s^o/B_s)^v B_s^v = (B_a^o/B_s^o)^v (B_s^o/B_s)^v \bar{p}_v \frac{E}{\pi} ,$$

where B_s^o = surface brightness at the center of the disk,

B_s = average surface brightness, and \bar{p}_v = visible geometric albedo. Thus the pressure is given by

$$P_{(mb)} = \frac{4 \times 10^{-3} g}{A_o p (\cos \theta)} \left[\frac{x M_1 + (1-x) M_2}{x \sigma_1^v + (1-x) \sigma_2^v} \right] \left[(B_a^o/B_s^o)^v (B_s^o/B_s)^v \bar{p}_v \right. \\ \left. - \frac{\lambda_v^2 \mathcal{N}_v i_o^v}{8\pi} \right] .$$

The application of this equation is restricted to particles small enough that their polarizing properties are similar to

those of molecules so that their brightnesses are additive.

In the visible (6200 \AA), the particles (if ice) must be smaller than $\sim 0.2 \mu$ diameter³³.

2.8 The Consequence of Atmospheric Absorption On Dollfus' Results

The presence of absorption in the Martian atmosphere would cause Dollfus' results to give too low a value to the air mass. The effect can be analyzed fairly simply.

If V is the phase angle and θ the zenith angle then light enters the atmosphere at an angle $(V - \theta)$ and leaves at θ (to the Earth). If τ is the total optical depth of the atmosphere then the ratio of the brightness of the atmosphere in the presence of absorption to the brightness when there is no absorption is

$$\left(\frac{1 - e^{-\tau s}}{\tau s}\right) = \frac{e^{-\tau s} - 1}{\ln(e^{-\tau s})} = \frac{p - 1}{\ln p},$$

where

$$s = \sec(V - \theta) + \sec \theta$$

and

$$p = e^{-\tau s}.$$

Thus the true brightness of the Martian atmosphere is the reciprocal of this quantity multiplied by the apparent brightness. Dollfus' polarization equation should now read

$$P(V, \lambda, \theta) = P_s(V) + \frac{B_a}{B_s} \cdot \frac{\sin^2 V}{2(B_V/B_0)} \cdot \frac{1}{(B_\theta/B_0) \cos \theta} \left(\frac{\lambda_0}{\lambda}\right)^4 \cdot \frac{p - 1}{\ln p}.$$

Opik²⁵ deduced the same correction factor. If his values for the absorption are used then the value of this factor is approximately 1.5. There are several reasons for doubting the validity of the

absorption figures which Öpik gives and Dollfus believes that the absorption is much less than this (see page 31). Consequently, although it is appreciated that the presence of absorption in the Martian atmosphere will increase the value for the pressure deduced from polarimetric measurements, it is not possible to place a reliable figure on it. From the brief discussion on the blue haze it appears that there is some absorption present: from Dollfus' remarks the absorption is fairly small, appreciably less than Öpik's values: hence one might tentatively say that the effect on the pressure measurement is $\sim 20\%$ (as opposed to Öpik's 50%) and in this way make an allowance for uncertainty. This has been done in the error given for the deduced value of B_a/B_s and accounts for the asymmetry in the error figures.

2.9 The Effect of Particle Scattering on Ultraviolet Pressure Determinations

The average brightness of the atmosphere of Mars, due to simple Rayleigh scattering by two molecular atmospheric constituents, is

$$B_m = 2.12 \frac{p(\cos 0)}{4\pi} E \cdot h (n_1 \sigma_1^b + n_2 \sigma_2^b) ,$$

where:

E is the incident solar flux,

h is the normal thickness of atmosphere,

$p(\cos 0)$ is the Rayleigh phase function for opposition = 1.5,

2.12 is a correction factor for sphericity of the atmosphere,

n_1, n_2 are the number of molecules per unit volume for the two constituents, and

σ_1^b, σ_2^b are the Rayleigh scattering coefficients per molecule for the two constituents.

The brightness due to particulate scattering³² is given by

$$B_p = \frac{2.12 \lambda_b^2 \mathcal{N} i_o^b}{8\pi} ,$$

where

λ_b is the wavelength of scattered light (3300 Å),

\mathcal{N} is the number of particulate scatterers per cm²-column, and

i_o^b is the Mie scattering coefficient for backscatter from these particles in the ultraviolet.

The surface pressure is given by

$$P = \frac{gh}{A_o} (n_1 M_1 + n_2 M_2),$$

where M_1, M_2 are the gram molecular weights of the two constituents.

If the two gases are present in proportion such that $n_1 = n x$ and $n_2 = n (1-x)$, where n is the total number of molecules per unit volume, then,

$$P \left(\frac{\text{dyne}}{\text{cm}^2} \right) = \frac{4 \pi g}{2.12 A_o p (\cos \theta) E} \left[\frac{x M_1 + (1-x) M_2}{x \sigma_1^b + (1-x) \sigma_2^b} \right] B_m.$$

Since the ultraviolet surface albedo of Mars is very low, we can assume that the total brightness of the planet B_T is due to the atmosphere,¹⁸ i.e., $B_T = B_m + B_p$. Thus,

$$P \text{ (mb)} = \frac{4 \times 10^{-3} \pi g}{2.12 A_o p (\cos \theta) E} \left[\frac{x M_1 + (1-x) M_2}{x \sigma_1^b + (1-x) \sigma_2^b} \right].$$

$$\cdot \left[\frac{B_T}{B_L} - \frac{B_p}{B_L} \right] B_L,$$

where B_L = brightness of an equivalent Lambert surface = E/π ⁸⁵.

The pressure is then given by

$$P \text{ (mb)} = \frac{4 \times 10^{-3} g}{2.12 A_o p (\cos \theta)} \left[\frac{x M_1 + (1-x) M_2}{x \sigma_1^b + (1-x) \sigma_2^b} \right] \cdot \left[\bar{p}_b - \frac{2.12 \lambda_b^2 \mathcal{N} i_o^b}{8 \pi} \right],$$

where \bar{p}_b is the geometric albedo defined as the ratio of the brightness of the planet to that of an equivalent Lambert surface.⁸⁵ For \mathcal{N} particles per cm^2 -column suspended in an atmosphere composed of $2/3 \text{ N}_2 + 1/3 \text{ CO}_2$, the pressure is given by,

$$P (1/3 \text{ CO}_2 + 2/3 \text{ N}_2 + \mathcal{N}) = \left[22.2 - 4.53 \times 10^{-8} \mathcal{N} i_o^b \right] \text{ mb}.$$

Penndorf³² gives the Mie scattering coefficient $i_o^b \sim 0.151$ for backscatter from 0.2μ diameter ice particles at 3300 \AA . The presence of $\sim 7.1 \times 10^8$ particles per cm^2 -column which reduced the visible determination to 20 mb, reduces the ultraviolet determination to 17.3 mb.

2.10 The Agreement of Visible and Ultraviolet Pressure Determinations

We have previously (see Appendices 2.7 and 2.9) derived the expressions for the surface pressure on Mars in terms of the visible and ultraviolet albedos, with consideration given to particulate scattering. Both pressure expressions can be equated since the pressure must be independent of the wavelength of observation. Assuming that a single particle size and type is responsible for particulate scattering, we can solve for \mathcal{N} , the number of particles per cm^2 -column required to bring the results of the visible and ultraviolet observations into harmony. Setting these expressions equal we find that the particle concentration required is given by

$$\mathcal{N} = \frac{\left\{ \frac{\bar{p}_b}{2.12} - (B_a^\circ/B_s^\circ)^v (B_s^\circ/B_s)^v \bar{p}_v \left[\frac{x \sigma_1^b + (1-x) \sigma_2^b}{x \sigma_1^v + (1-x) \sigma_2^v} \right] \right\}}{\left\{ \frac{\lambda_b^2 i_o^b}{8\pi} - \frac{\lambda_v^2 i_o^v}{8\pi} \left[\frac{x \sigma_1^b + (1-x) \sigma_2^b}{x \sigma_1^v + (1-x) \sigma_2^v} \right] \right\}}.$$

Substituting the above result for \mathcal{N} in either of the expressions for surface pressure yields a value consistent with both sets of observations. This pressure is given by

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The fact that this ratio is approximately constant suggests that the same compatible pressure exists for all particle sizes (small enough that they do not affect the polarization) and therefore for any distribution of particles sizes although the numbers of particles required for compatibility varies.

Evaluating the above expression, with the values of the parameters given earlier and in the text, gives a pressure of

$$P_{v,b} = 16.8 \text{ mb}$$

which satisfies both the visible and ultraviolet determinations.

For 0.2μ diameter ice particles we require

$$\mathcal{N} \cong 7.8 \times 10^8 \text{ per cm}^2\text{-column for compatibility.}$$

3.1 The Effect of Saturation on the CO₂ Abundance

The criteria for the applicability of the weak line model depend on the relative importance of the pressure and Lorentz and Doppler half-widths³⁴. In Fig. A-6, these half-widths are shown for temperatures from 100°K to 300°K, and for total gas pressures from one to 100 mb. The collision half-width at STP was taken as 0.10 cm^{-1} in order to correspond with the values in KMS. A value of 0.064 cm^{-1} has been measured for the $15\mu \text{ CO}_2$ band⁴¹, which, if applicable to the $5\mu_3$ bands, would shift all the collision half-widths down by about 35 percent. Although the half-width is not precisely known, the general conclusions that follow from Fig. A-6 are not greatly dependent on which value of the half-width is used. At temperatures in the vicinity of 200°K, the Lorentz and Doppler half-widths are of the same order of magnitude for pressures of approximately 60 mb to 100 mb. However, if the total pressure is as low as 10 to 20 mb, the Doppler width is about four to five times the collision half-width.

If the weak line approximation applies, the expression for the equivalent width is the same whether collision or Doppler broadening is more important. For pressure broadened lines, the weak line approximation is valid within q percent for $x = Su/2\pi b \leq 0.02q$ ³⁴. Similarly, the weak line approximation

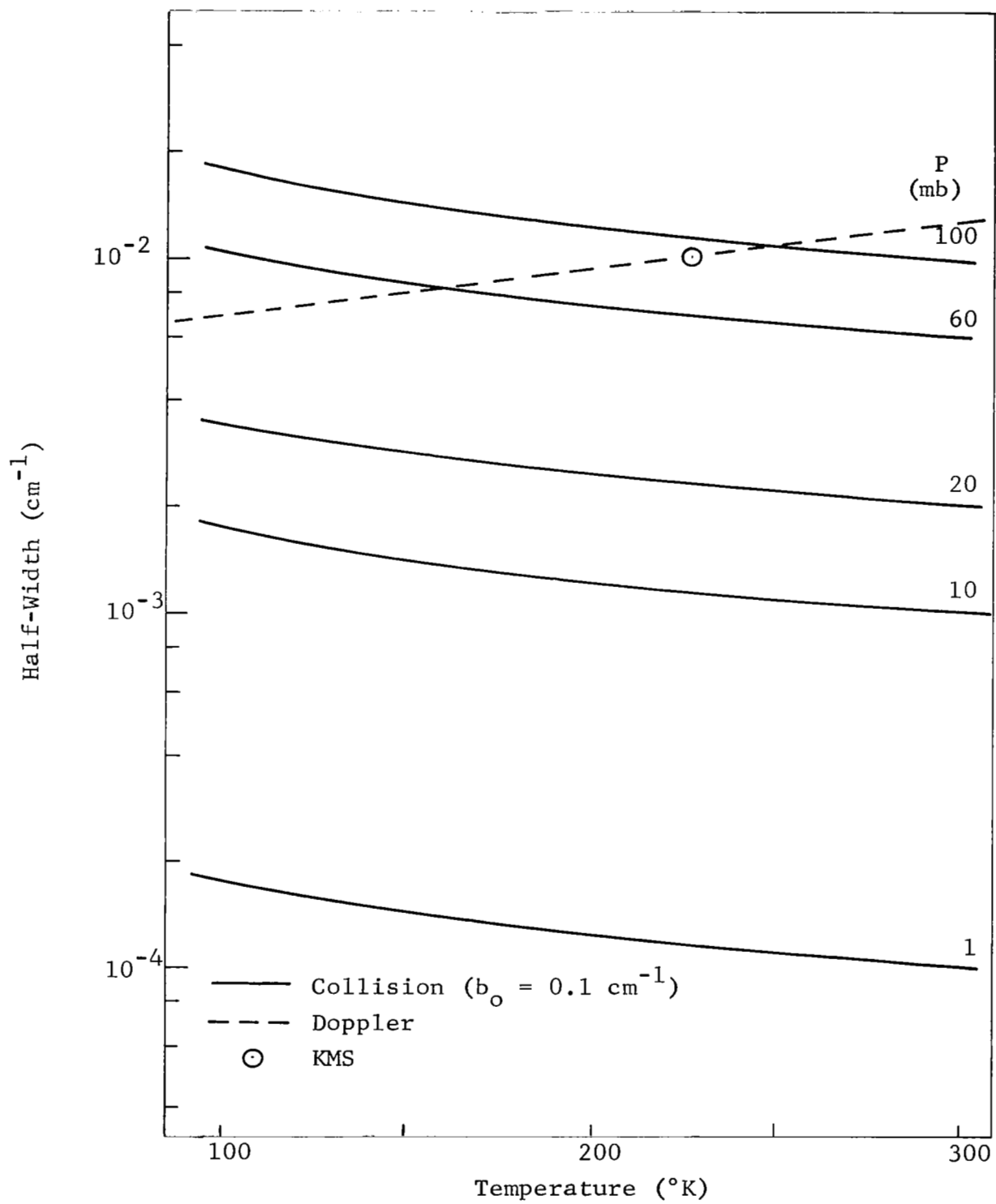


Fig. A-6 CO_2 Lorentz and Doppler Line Half-Width vs. Temperature

is valid within q percent for purely Doppler broadened lines if $x_D = \left[(\ln 2) / \pi \right]^{1/2} (S_u / b_D) \leq 2^{1/2} q / 50$. The values of q for collision and Doppler broadened lines are shown in Fig. A-7 for pressures up to 100 mb. At 200°K the weak line approximation is valid within 10 percent for Doppler broadened lines and for collision broadened lines at pressures greater than about 40 mb. Since the half-widths shown in Fig. A-6 indicate that the Doppler width at 200°K is \geq the collision half-width for pressure below 60 mb, the purely Doppler broadened line should, as suggested by (KMS), provide an upper limit for the effects of saturation. Furthermore, the saturation should be sufficiently small that the abundance obtained from the weak line approximation should be in error by no more than about 10 percent. Thus the abundance may be the order 10 percent higher than was obtained by considering the combined effects of collision and Doppler broadening. As indicated by KMS, this is conveniently accomplished with the aid of tables given by Harris⁴³, and the abundance obtained in this manner is 7-1/2 percent higher than that given by the weak line approximation.

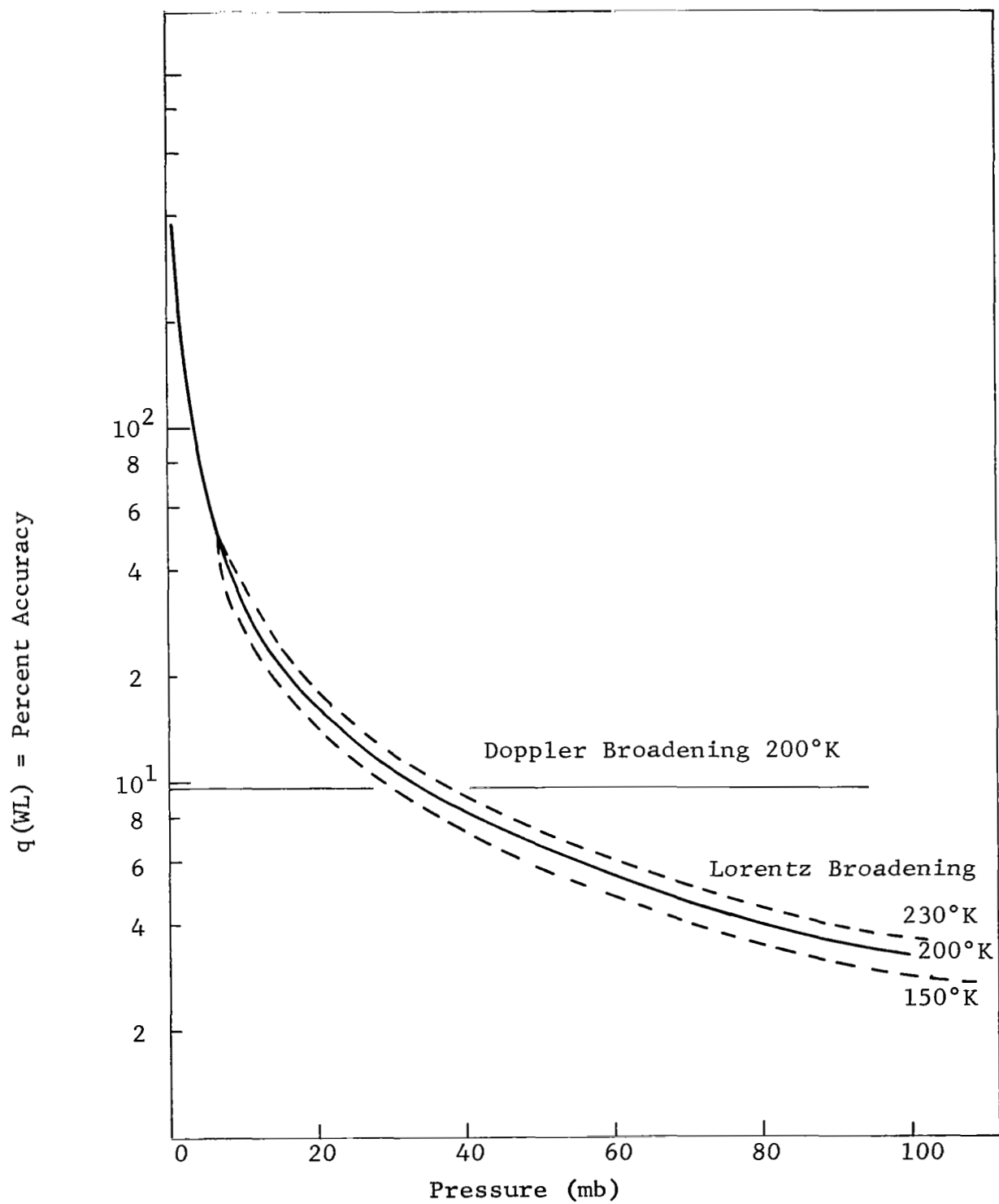


Fig. A-7 Accuracy of Weak Line Approximation

3.2 Uncertainty in the CO₂ Abundance

The general expression for the relative error of a quantity N which is a function of variables u_1, u_2, \dots, u_n , is

$$E_R = \frac{\Delta N}{N} = \sum_{i=1}^n \frac{N}{u_i} \frac{u_i}{N} . \quad (2.1)$$

For the relative error in the CO₂ abundance determined with the weak line approximation, this expression becomes

$$\frac{\Delta W}{W} = \frac{\Delta W}{W} + \frac{\Delta n}{n} + \frac{\Delta S}{S} . \quad (2.2)$$

Since KMS suggest the upper limit for the equivalent width of 3.8 m $\overset{\circ}{\text{A}}$ is between 5 and 6 m $\overset{\circ}{\text{A}}$, a value of 5.5 m $\overset{\circ}{\text{A}}$ was used for the upper limit, and assuming the uncertainty is symmetrical about the value of 3.8 m $\overset{\circ}{\text{A}}$, the relative error $\Delta W/W$ is about 0.90. Although no error is associated with the integrated absorption given by Rank et al., it is obvious from the data shown in that paper and from similar measurements made on other absorption bands that the uncertainty is not negligible. It seems reasonable to assume $\Delta S/S$ is at least 0.10, i.e., the intensity is accurate to ± 5 percent. While the air mass may in principle be precisely calculated, the judgment required to determine this value suggests the accuracy is no better than ± 10 percent. If these relative errors are inserted in Eq. (2.2), the result is

$\Delta w/w = 1.2$, i.e., the relative error in the abundance is on the order of ± 60 percent. The CO_2 abundance at 200°K can then be expressed as 43 ± 25 m-atm.

An analysis of the errors involved in Owen's CO_2 abundance calculation follows the same method used in determining the uncertainty in the KMS abundance. In this case the relative error, accounting only for the uncertainty in the laboratory measurement and a ± 10 percent uncertainty in the air mass, is $\Delta w/w = 0.57$, which implies that at 200°K , $w = 46 \pm 13$ m-atm. The additional ± 7 m-atm added by Owen to account for the temperature correction and the question of overlapping rotational lines is sufficient and the error estimate of ± 20 m-atm is probably realistic. However, since the final value is obtained on the assumption that overlapping does occur, the uncertainty is no longer symmetrical and this value should probably be given as $46 (+15, -20)$ m-atm.

The assignment of errors to the results of Hanst and Swan proceeds along the same lines as for the other two determinations. These authors give 20 percent as a "conservative estimate" for the probable error in their measurement of S which they attribute primarily to the error in measuring areas and heights of the absorption curves. If we accept an error of $\pm 45\%$ in the determination of the equivalent widths of the CO_2 lines in the Martian spectrum, it seems necessary to increase the Hanst and Swan figure to at least $\pm 30\%$ to allow for the possibility of a systematic error in the measurement of the

continuum. We then apply the analysis outlined above to obtain the relative error in w , which is found to be $\pm 85\%$. The CO_2 abundance at 200°K is then expressed as 21 ± 18 m-atm.

3.3 Uncertainty of the Martian Surface Pressure

a) For Sinton's 2μ CO_2 absorption measurements, the error includes contributions from the value of 1.86 used to compare Martian and telluric absorption as well as the CO_2 abundance in both atmospheres, the pressure in the Earth's atmosphere, and the air mass for the telluric atmosphere that is appropriate for the observations. An estimate of the accuracy for this value 1.86 was obtained directly from Sinton's data (Fig. A-8) by a least squares fit of a straight line to his observations, and a calculation of the probable error for the deviation of the observations from this straight line. The results suggest that the relative error in this quantity is approximately 35 percent. (There is a slight inconsistency here, since the other relative errors were extreme limits; thus the resulting uncertainty will be somewhat lower than if the upper limit were used.) It was shown above that the error associated with the Martian CO_2 abundance is approximately ± 65 percent, and if a modest figure of 2 percent is assumed for each of the relative errors of the telluric atmospheric pressure, CO_2 abundance, and air mass, the relative error for the pressure is $\Delta p/p = 1.8$ or ± 90 percent. No error is included for the HBW factor that accounts for the effectiveness of self-broadening, but in this case that error would not have a significant effect on the final result. It is

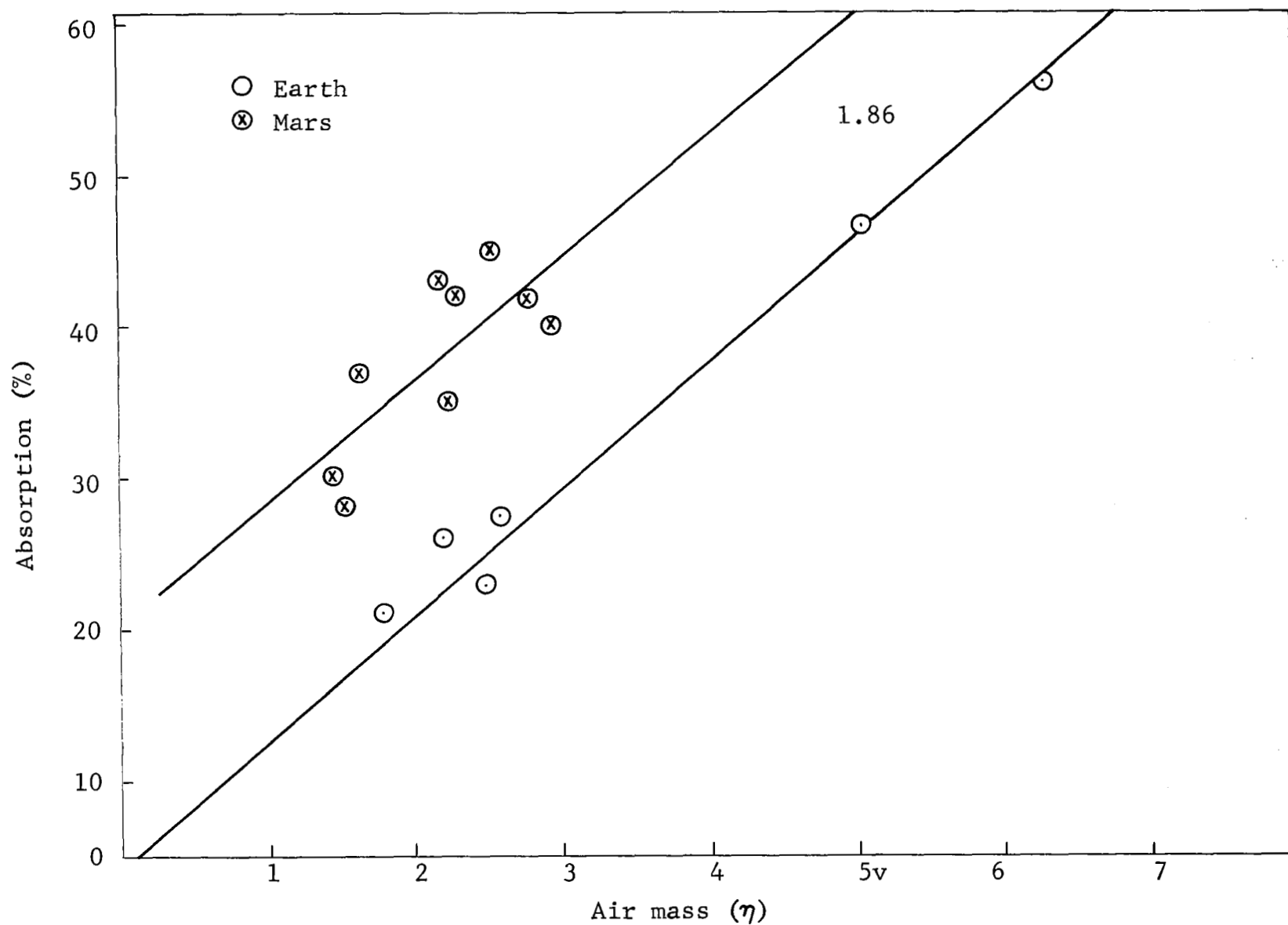


Fig. A-8 Absorption of 2.06μ CO_2 Bands from Sinton (Ref. 45)

believed that the errors assumed for the telluric pressure, CO₂ abundance, and air mass are low, so that this relative error is conservative.

It is not completely obvious that the temperature dependence of the rotational line intensity should be omitted in this calculation. Sinton's statement that the Martian absorption is equivalent to an increase of 1.86 telluric air masses refers to the band center and not the entire band. If the Boltzmann factor were included, the pressures would be reduced by at most eight percent.

b) The same analysis applied to the pressure obtained by comparison of Kuiper's Martian spectra and laboratory spectra requires an additional estimate for the error associated with the HBW determination of the relative effect of CO₂ self-broadening and nitrogen gas broadening. Although a correction for this effect is made in all three pressure determinations, in the other two cases the error associated with this quantity is negligible. However, in this case the effective Martian pressure is directly proportional to the effectiveness of self-broadening, and the uncertainty in this quantity is directly reflected in the final value for surface pressure.

c) Kuiper's 2 μ CO₂ equivalent widths. For this calculation the only known error contribution is for the Martian CO₂ abundance. The following estimates of the errors are considered conservative and were used to evaluate the uncertainty of the derived value of the Martian surface pressure.

- | | | |
|----|------------------------------------|-----------|
| 1) | Martian CO ₂ abundance | \pm 65% |
| 2) | Martian air mass | \pm 10% |
| 3) | Telluric CO ₂ abundance | \pm 1% |
| 4) | Telluric air mass | \pm 1% |
| 5) | Telluric atmospheric
pressure | \pm 1% |
| 6) | Martian equivalent width | \pm 5% |
| 7) | Telluric equivalent width | \pm 5% |

3.4 The General Behavior of Absorption as a Function of Pressure and Optical Density

Some insight into the significance of the results in this report can be gained by considering the general behavior of absorption as a function of pressure and optical density. To facilitate this discussion, a plot of absorption vs. a quantity proportional to the product of pressure times optical density from a paper of G. N. Plass⁵⁰ is reproduced in Fig. A-9. In Plass' notation, $\beta = 2\pi b/d$ and $x = Su/2\pi b$, where b is the line half-width, d is the line spacing, S is the rotational line intensity, and u is the optical density of the absorbing gas. The quantity $\beta^2 x$ is proportional to pu because of the dependence of line half-width on the pressure. The curves for constant pressure are represented by $\beta = \text{constant}$, and for constant optical density by $\beta x = \text{constant}$.

The absorption increases linearly with optical density until absorption is nearly complete near the centers of the strongest spectral lines. As optical density is further increased, absorption is proportional to the square root of the optical density. For very large optical densities the spectral lines begin to overlap, absorption increases very slowly with optical density, and eventually becomes complete. At low pressures absorption increases as the square root of the pressure. As the pressure increases, the spectral lines are

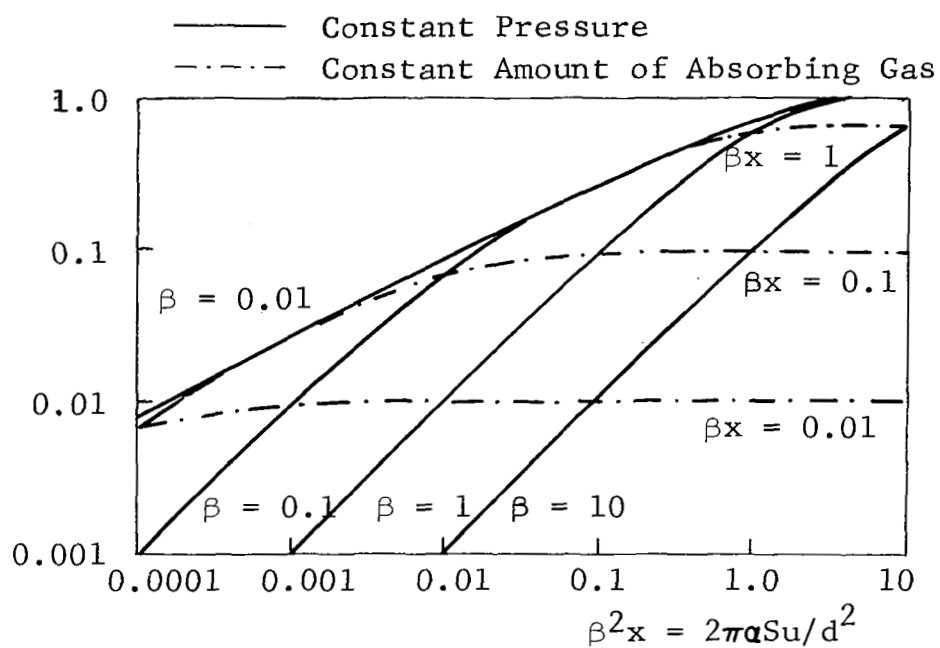


Fig. A-9 Absorption vs. $\beta^2 x \sim pu$ for the Elsasser Model from G. N. Plass (Ref. 50)

sufficiently broadened so that absorption is no longer complete at the line centers, and absorption increases as a smaller power of pressure. At a high pressure, which is determined by the number of absorbing molecules and the distance between spectral lines, the absorption is independent of pressure. In general the absorption does not vary as rapidly with pressure as it does with optical density.

3.5 Martian Surface Pressure Determined with the Square Root Approximation and the Pressure Dependent Extrapolation

The equivalent widths corresponding to Martian CO₂ abundances were determined by assuming the equivalent widths are in the square root region, for which $\Delta \log W = 0.217 \ln u_1/u_0$, where u_1 is the abundance on Mars and u_0 is the abundance from which the extrapolation is made. For the 100 percent CO₂, the points for 150 m-atm fall approximately on the curve given in the (OK) paper (Fig.A-10). Although a slightly different line could be drawn through these points, no significant change in pressure would result. However, for the 10 percent CO₂ and 25 percent CO₂, the points deduced in this same manner do not fall on the curves given by (OK). For the 25 percent CO₂ there is fair agreement at the higher pressures, and it is conceivable that some correction was made at lower pressures on the assumption that the absorption was not on the square root portion of the curve. The extrapolated values of equivalent width for the 10 percent CO₂ are even further from the curve given by (OK). From the comments in the paper, it is not possible to determine how the authors arrived at their published values for the curves representing the Martian CO₂ abundance. Although the details of the method are not available, it has been stated⁴⁹ that some

adjustment was made to account for the fact that the square root approximation does not appear to be valid in the pressure region of interest (~ 20 mb).

The results obtained with the pressure dependent extrapolation are shown in Figure A-11. For 100% CO_2 the square root approximation yields approximately the same curve given by (OK), and an effective pressure of 4.8 mb. However, if the pressure dependence of $\Delta \log W$ is considered, the effective pressure is 6.7 mb, which implies a surface pressure of 13.4 mb as compared to the 9.6 mb given by (OK). The equivalent width data for 10 percent CO_2 and 25 percent CO_2 are somewhat more difficult to analyze in this manner, because it is not clear exactly how (OK) arrived at the curves that correspond to the Martian abundance, and there is no experimental data that would indicate the equivalent width dependence on optical density for pressures lower than 20 mb. For the 25 percent CO_2 gas mixture, three values of surface pressure can be obtained: (1) the curve in (OK) yields 16 mb, (2) the square root extrapolation gives 12 mb, and (3) the pressure dependent extrapolation yields 14 mb. For the 10 percent CO_2 , the (OK) curve gives 19 mb, while a surface pressure as high as 24 mb might be obtained from the pressure dependent calculation.

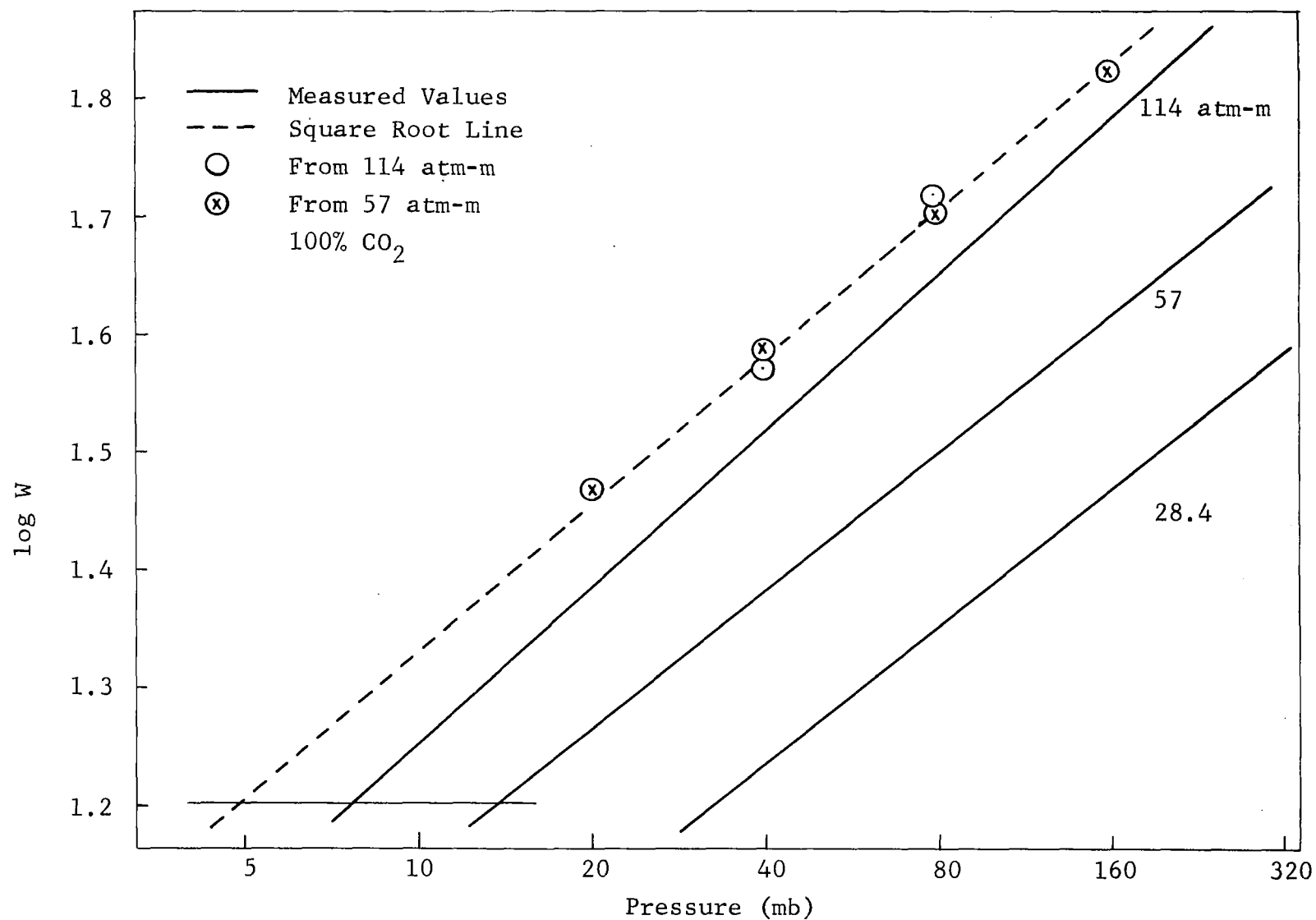


Fig. A-10a Extrapolation of Equivalent Widths to Martian CO₂ Abundance Using Square Root Approximation

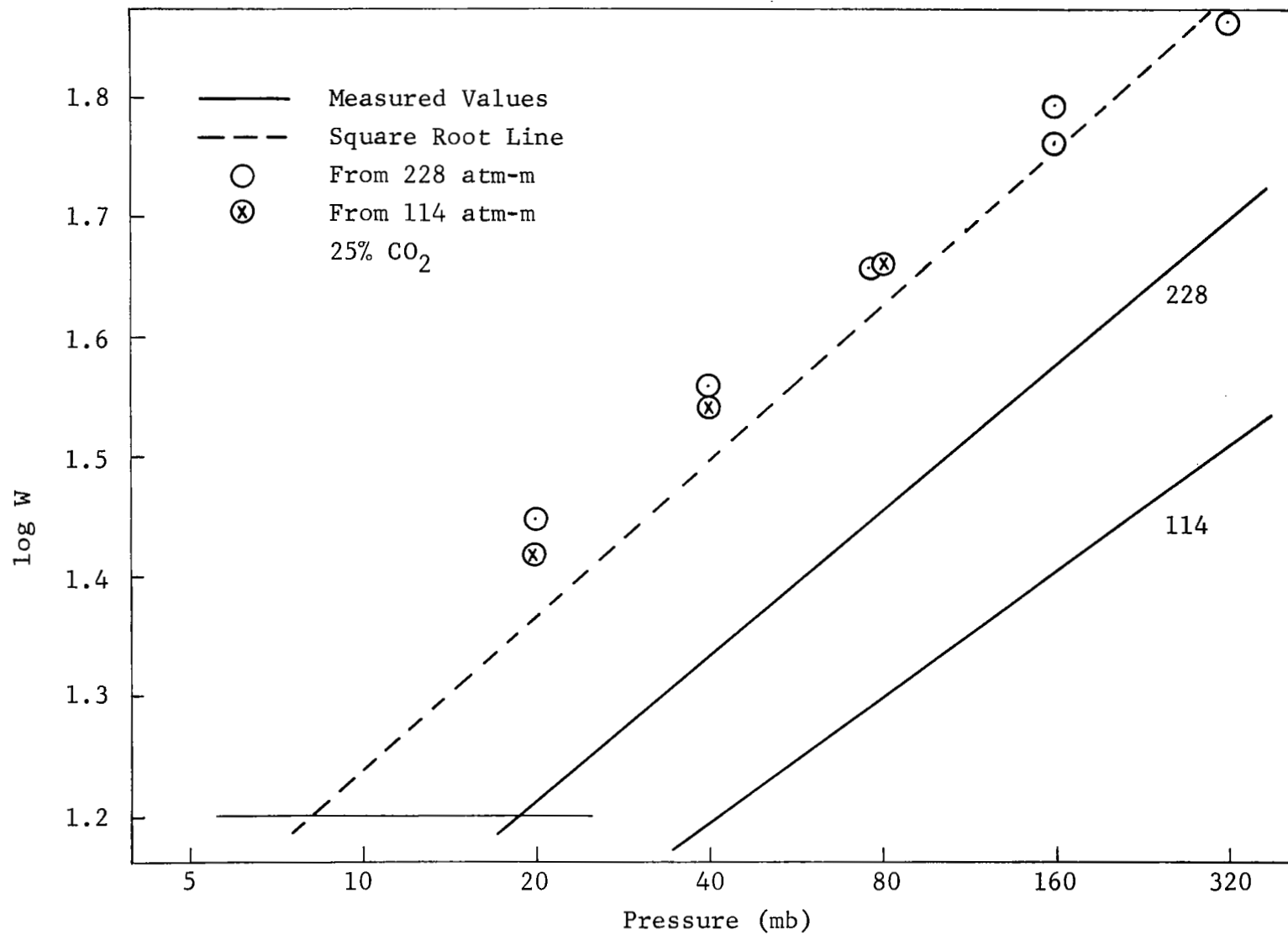


Fig. A-10b Extrapolation of Equivalent Widths to Martian CO₂ Abundance Using Square Root Approximation

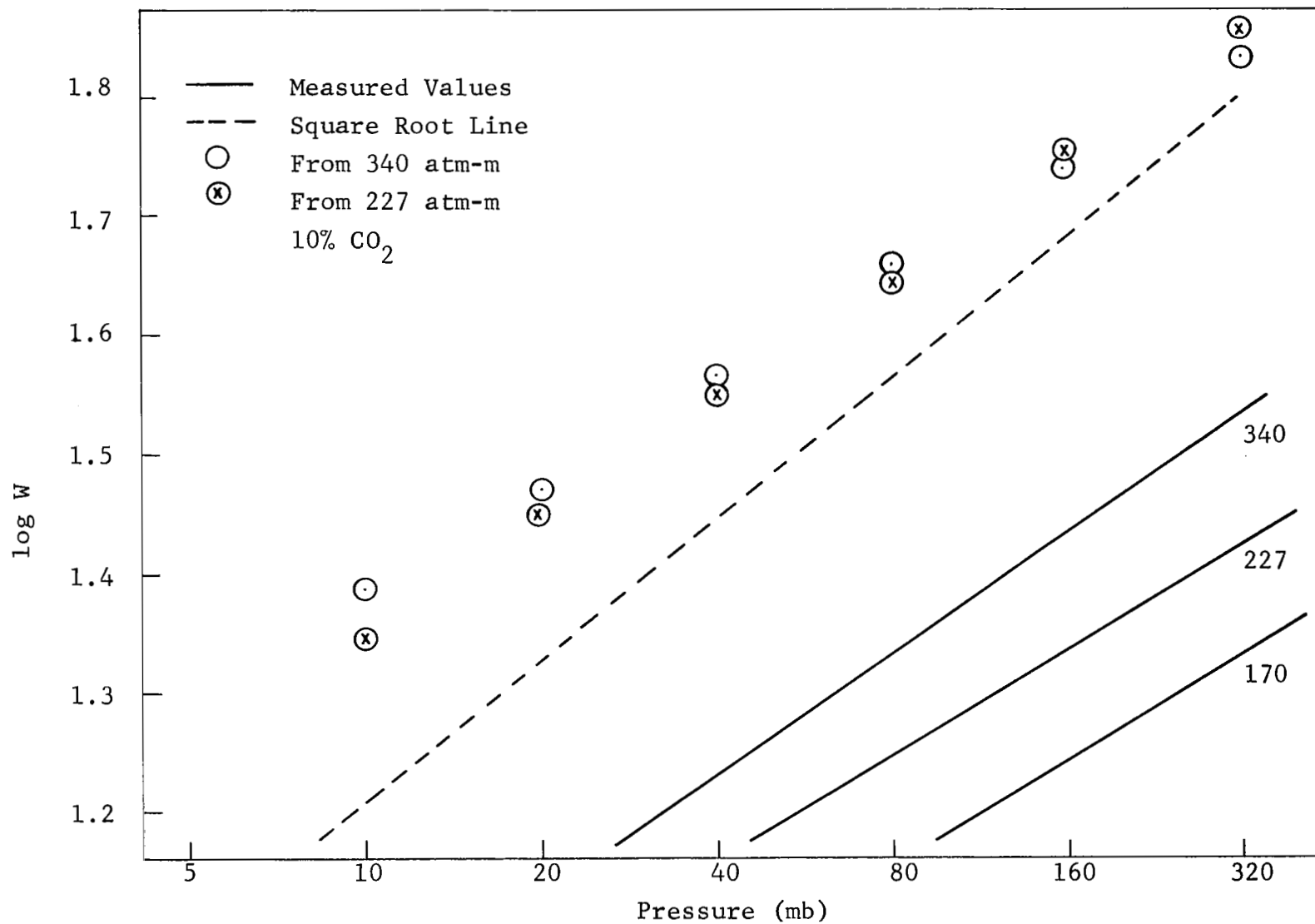


Fig. A-10c Extrapolation of Equivalent Widths to Martian CO₂ Abundance Using Square Root Approximation

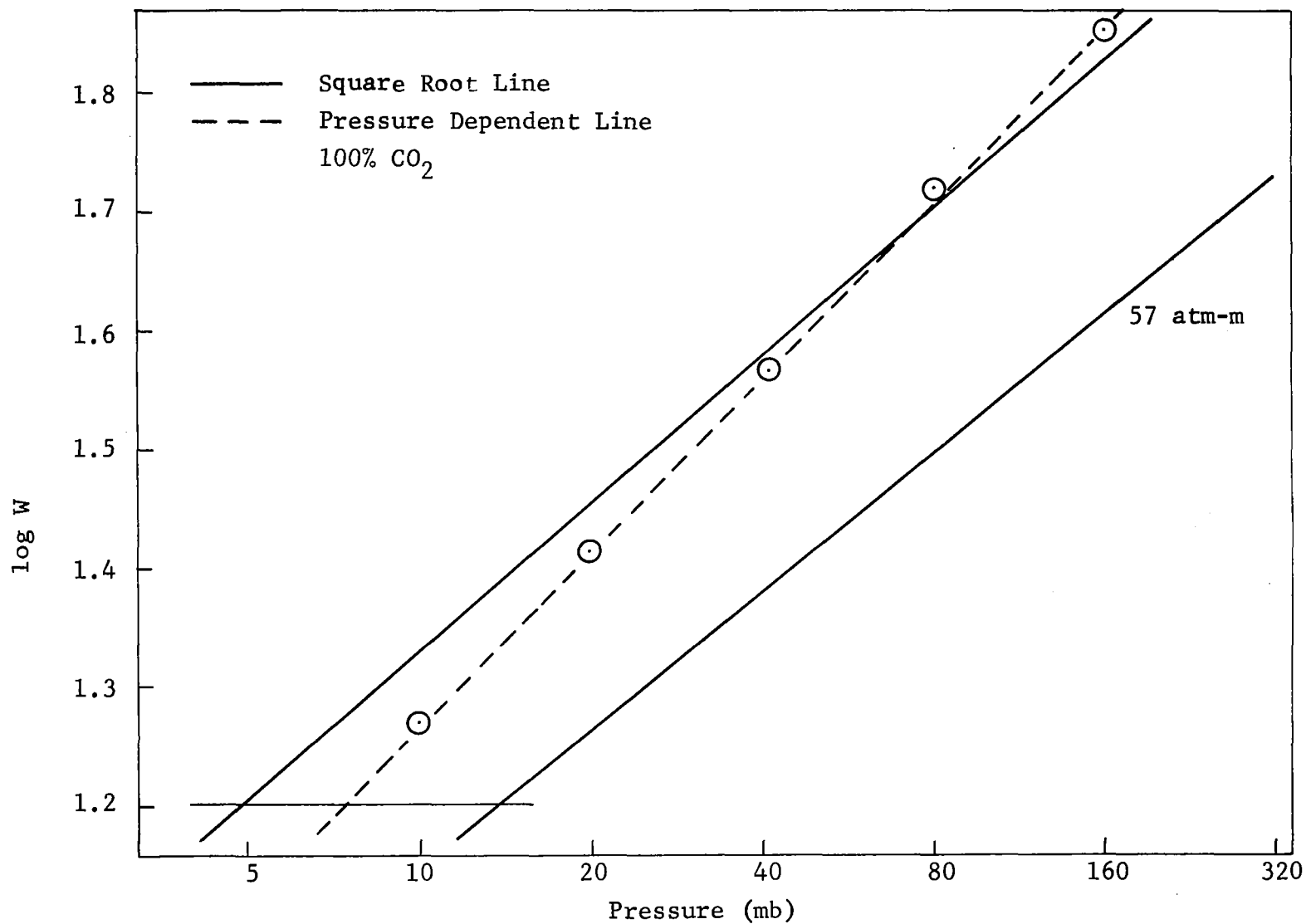


Fig. A-11a Extrapolation of Equivalent Widths to Martian CO₂ Abundance Using Pressure Dependent Method

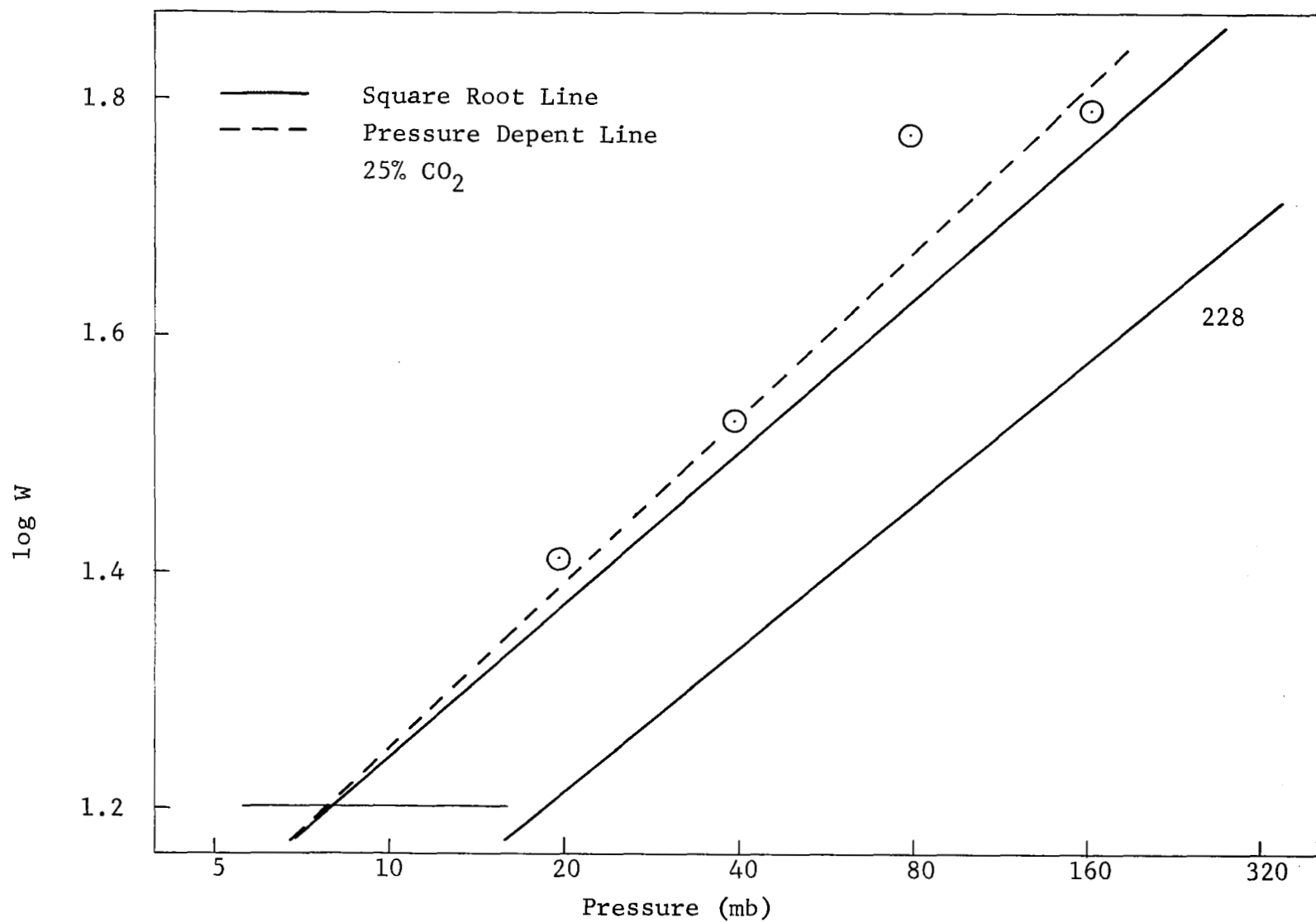


Fig. A-11b Extrapolation of Equivalent Widths to Martian CO₂ Abundance Using Pressure Dependent Method

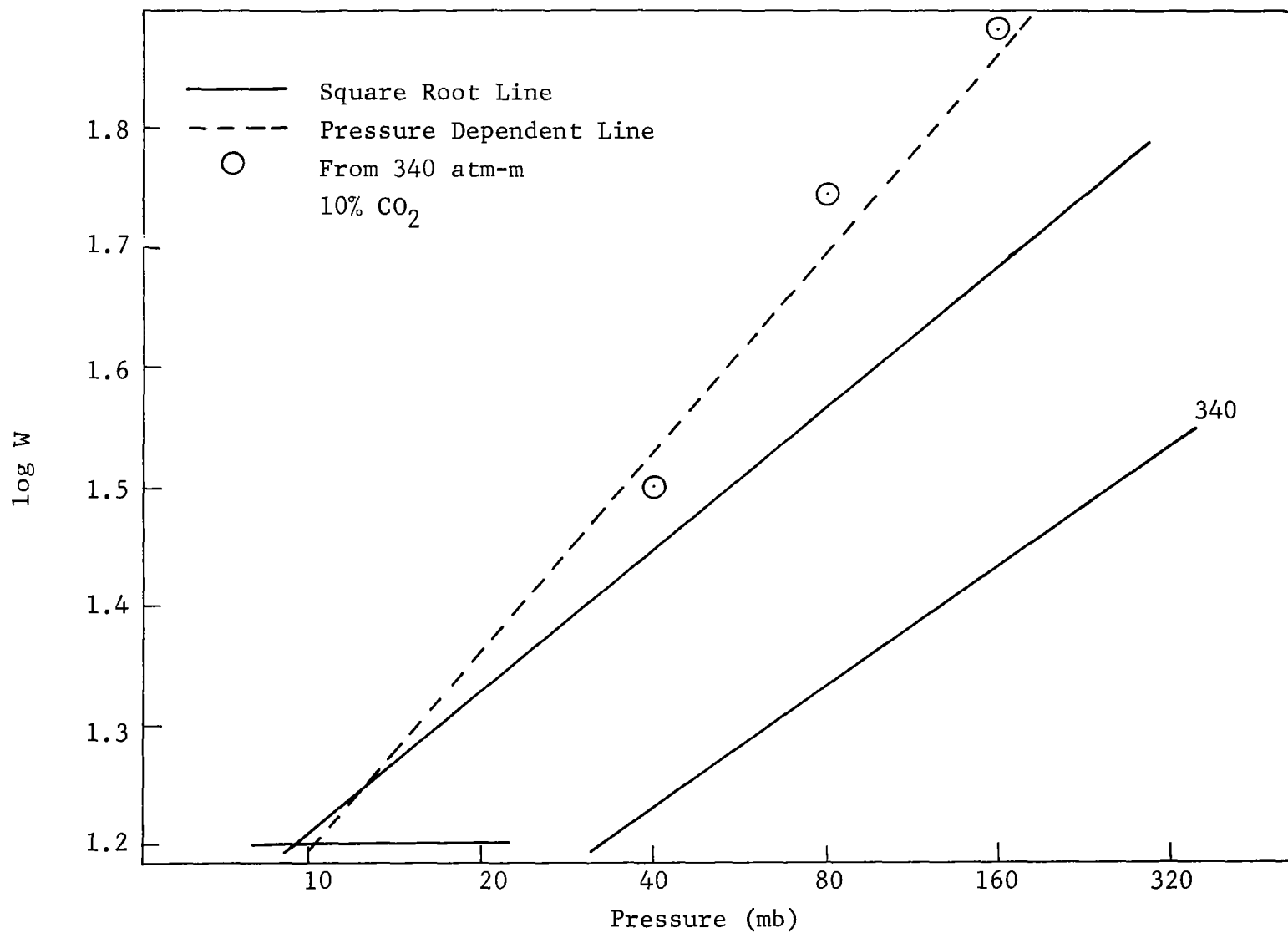


Fig. A-11c Extrapolation of Equivalent Widths to Martian CO₂ Abundance Using Pressure Dependent Method.

3.6 Uncertainties in the Pressure Derivation of Moroz

Moroz' original derivation of relations between u and p based on the absorption strengths of two of the Martian CO_2 bands and the Elsasser band model led to the following results:

$$\begin{array}{ll} 1.6\mu \text{ band} & u_p = 170 \pm 40 \\ 2.06\mu \text{ band} & u_p = 184 \pm 20 \end{array}$$

From these numbers he adopted a mean of $u_p = 175$ and used the KMS value for $u = 55 \pm 20$ m-atm $= 11 \pm 4$ gm/cm². If one assumes that Moroz set $u_p = 175 \pm 30$ and then computed the limits for these numbers, one obtains

$$\begin{array}{l} (\text{lower limit}) \quad p = \frac{145}{15} = 10 \text{ mb} \\ (\text{upper limit}) \quad p = \frac{205}{7} = 30 \text{ mb} \end{array}$$

which is consistent with his result of $p = 15^{+15}_{-5}$ if one further assumes that he has rounded off $\frac{175}{11}$ to 15 (rather than 16).

These assumptions appear to be reasonable procedures to be followed with the available material. Moroz relied on a value of the NTP half width obtained from Kaplan⁵⁷, which we verified in the work of Goldberg⁵⁸ and Goody⁵⁹. Finally, the value Moroz used for the spacing of the rotational lines in the Elsasser model was checked against measurements of the telluric $1.6\mu \text{ CO}_2$ band⁶⁰. We have shown that a better value for the telluric CO_2 abundance and the inclusion of a temperature correction in γ lead to values of P which are lower than the

value given by Moroz by an amount which depends on the adopted value of u . We did not use the same technique as Moroz in applying the Elsasser model to the observations since we relied on tables of the essential parameters compiled by Kaplan⁵⁴ and Wark and Wolk⁵⁵. The uncertainty cannot be any less than the amount given by Moroz since our results rely on the same observational data. On this basis we find

$$a) \ u = 55 \text{ m-atm}$$

$$P = 8 \begin{matrix} +8 \\ -3 \end{matrix} \text{ mb}$$

$$b) \ u = 45 \text{ m-atm}$$

$$P = 10 \begin{matrix} +10 \\ -4 \end{matrix} \text{ mb}$$

It is not possible to check the uncertainties Moroz assigns to his derivations of the relations for (up) without repeating the technique as he did it. This procedure was excluded by lack of available time. As an alternative, we have considered the extreme values corresponding to his calculations as representing the worst possible case. In addition, we have added an uncertainty of ± 0.02 to his value of the absorption, A , (based on measurements made by Courtoy⁵⁶) to account for a $\pm 15\%$ uncertainty in the band half-width and an equal uncertainty in the measured equivalent width. Correcting A for the lower temperature anticipated in the Martian atmosphere we have $A = 0.08 \pm .02$. If we then adopt the lower abundance (45 m-atm) as being most probable, our final revised value becomes

$$P = 13 \begin{matrix} +25 \\ -8 \end{matrix} .$$

It should be stressed that these error limits are less well determined than those given for the KMS and OK papers and thus should not be given the same weight.

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